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HTGR "Green" Rod Intercomparison

I. Hydrogen Assay

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HTGR "GREEN" ROD INTERCOMPARISON

I. HYDROGEN ASSAY

by

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ABSTRACT

A ^{252}Cf hydrogen monitor has been used to determine the hydrogen content of each of the 144 unfired ("green") fuel rods being circulated in the New Brunswick Laboratory fuel measurement evaluation program. The monitor was calibrated with standards fabricated by Los Alamos Scientific Laboratory (LASL) Analytical Chemistry Group, CMB-1. Measurements were made relative to these standards and overall accuracies of $\pm 3\%$ were achieved.

I. INTRODUCTION

A major problem in the fast neutron assay of High Temperature Gas-cooled Reactor (HTGR) unfired ("green") rods is the presence of hydrogen (H), which moderates the average energy of the interrogating flux and thereby changes the response of the system. Preliminary work has shown that this effect enhances the response by about 25% for the 150-mg H content of the rods and 10% for the 450-mg H content of the polyethylene encapsulation provided for the HTGR fuel measurement evaluation program, sponsored by New Brunswick Laboratory (NBL). To make this correction with confidence, accurate measurement of the hydrogen content must be made. To this end, the hydrogen monitor¹ has been calibrated and used to measure H content of these rods.

The rods are right circular cylinders 1.4 cm in diameter and 5.0 cm high composed of TRISO-coated UC_2 and ThO_2 beads embedded in a carbon matrix. Table I lists the characteristics of the three blends that are under consideration in the measurement evaluation program. For the intercomparison each rod is encapsulated in a sealed polyethylene vial. Section II describes the experimental apparatus and procedures. Section III develops the formalism of

TABLE I
HTGR UNFIRED ("GREEN") RODS' CHARACTERISTICS

Blend	Average Mass (g)	Nominal ^{235}U (g)	Nominal Th (g)	Nominal H (g)
12(A)	13.6	0.160	3.478	0.135
13(B)	14.8	0.120	4.653	0.141
14(C)	13.8	0.290	3.478	0.136

relative measurements and the associated error analysis and treats the reduction of data to relative responses. The response of the hydrogen monitor to standards and the least squares fitting of these data to produce a "best" set of calibration parameters and variance-covariance matrix is the subject of Sec. IV. Analysis of the HTGR data is covered in Sec. V, and Sec. VI summarizes the results and conclusions.

II. EXPERIMENTAL

The hydrogen monitor is described in Ref. 1. Briefly, it is a steel cube with a ^{252}Cf source and two ^3He detectors embedded near its center. Hydrogen-bearing samples are introduced into a chamber located near the source and detector, and the enhancement in ^3He count rate caused by moderation of the fission neutron spectrum is a measure of the hydrogen content of the sample. Conventional electronics, including gain stabilization and pulse pileup rejection, is used to generate pulse-height spectra from the ^3He detectors in a multichannel analyzer (MCA). To monitor pileup and deadtime loss, constant amplitude pulses from a periodic pulse generator are continuously injected into the preamp. A typical spectrum is shown in Fig. 1. Four regions, corresponding to the thermal peak area, the pulser peak area, and two areas adjacent to the pulser peak that are taken as estimates of the background under the pulser peak, comprise the raw data collected for each run. The summation intervals for these areas are indicated in the figure.

Data were acquired in 800-s (MCA live-time) intervals. A background run without hydrogen in the chamber was followed by four to seven runs with

Fig. 1.

Pulse height spectrum from the hydrogen monitor. The following summation intervals are indicated: N--Thermal ^3He (n,p) peak; P--Pulser peak; B1 and B2--Background estimates for P.

standards and/or unknown samples in the chamber. A day's running was comprised of four to seven such sequences.

III. TREATMENT OF DATA

A. Relative Measurement Formalism

In the region of interest, the response of the hydrogen monitor can be represented by the expression

$$R = \sum_{i=1}^n A_i X_i, \quad (1)$$

where $X_1 = 1.0$ and the remaining X_i 's are the contents of a sample, including hydrogen, which perturb the response. The calibration problem lies in

deciding, which sample characteristics (X_i) produce the largest perturbations, fabricating standards with these characteristics accurately known, and determining the A_i 's by accurate measurement of the standards responses and least squares fitting of them. In principle, the instrument can then be used to measure hydrogen in unknowns by the relation

$$H^U = (R^U - \sum_{\substack{i=1 \\ i \neq H}}^N A_i X_i^U) / A_H, \quad (2)$$

as long as the perturbing constituents X_i^U are closely enough matched to the constituents of the standards that their respective effects on the response are approximated by the assumed linear relationship. The uncertainty in the result of such an assay is

$$\begin{aligned} \sigma(H^U)^2 = & A_H^{-2} \left[\sigma(R^U)^2 + \sum_{i \neq H} A_i^2 \sigma(X_i^U)^2 \right. \\ & + \sum_{i \neq H} \sum_{j \neq H} X_i^U X_j^U \text{cov}(A_i, A_j) \\ & + 2H^U \sum_{i \neq H} X_i^U \text{cov}(A_i, A_H) \\ & \left. + (H^U)^2 \sigma(A_H)^2 \right], \quad (3) \end{aligned}$$

where $\sigma(Y)$ is the relative standard deviation (1 sigma) associated with the variable Y , and $\text{cov}(A_i, A_j)$ is the element of the variance-covariance matrix corresponding to the covariance of parameters A_i and A_j [$\text{cov}(A_i, A_i) = \sigma(A_i)^2$]. The uncertainty is written in the above form to show its explicit dependence on $\sigma(A_H)^2$ and $\text{cov}(A_i, A_H)$.

A second technique for determining hydrogen with this instrument is to run standards along with unknown samples. In this case

$$H^U = H^S (R^U - \sum_{i \neq H} A_i x_i^U) / (R^S - \sum_{i \neq H} A_i x_i^S) \quad , \quad (4)$$

where H^S is the hydrogen content of the standard, R^S is its response, and x_i^S its perturbing constituents. For this case, the uncertainty is

$$\begin{aligned} \sigma(H^U)^2 = & \left[(H^S)^2 / D(S)^2 \right] \left[\sigma(R^U)^2 + \sum_{i \neq H} A_i^2 \sigma(x_i^U)^2 + (H_U/H_S)^2 \sigma(R^S)^2 \right. \\ & \left. + (H_U/H_S)^2 \sum_{i \neq H} A_i^2 \sigma(x_i^S)^2 \right] + \left[D(U)/D(S) \right]^2 \sigma(H^S)^2 \\ & + \sum_{i \neq H} \sum_{j \neq H} \left[x_i^U / D(U) - x_i^S / D(S) \right] \left[x_j^U / D(U) - x_j^S / D(S) \right] \text{cov}(A_i, A_j) \quad , \quad (5) \end{aligned}$$

with $D(T) = R^T - \sum_{i \neq H} A_i x_i^T$. Note the absence of dependence on variances or covariances of A_H and that for well-matched unknowns and samples ($x_i^U = x_i^S$) the coefficient of $\text{cov}(A_i, A_j)$ tends to vanish.

B. Reduction to Responses

The response for a given sample is the ratio of loss-corrected thermal peak area obtained with the sample in to the same area with no sample (a background). The absolute loss rate was 25% and a relative loss correction was applied by normalizing each subsequent run to the first background run of the day. Each loss-corrected peak was the uncorrected peak area divided by the ratio of net pulser peak for that run to net pulser peak for the first background.

To compensate for ^{252}Cf decay and possible long-term electronic drift a function linear in the time of day was linear-least squares fit to the backgrounds. This function was then used to generate the responses for the individual assays at the times they were taken. The variance-covariance matrix from the fit provided the statistical uncertainties associated with each assay.

IV. CALIBRATION

A. Standards

Calibration standards with characteristics resembling those of the HTGR rods were generated and are listed in Table II. Standards 1-6 are fabricated by LASL Analytical Chemistry, Group CMB-1, and are comprised of U_3O_8 mixed with dextrose and graphite. The ^{235}U content was nominally 100, 200, and 300 mg with quoted accuracies of ± 0.01 mg and the hydrogen content was 100 and 150 mg ± 0.01 mg. The mixture's primary encapsulation was a glass "1 dram" vial with a Bakelite cap. Sufficient graphite was added to each standard to give it a constant (20 ± 1 mm) fill height. To make the resemblance to HTGR rods closer, a secondary encapsulation of a "2 dram" polyethylene vial, similar to those that provide primary encapsulation for the HTGR rods, was provided for each standard. The hydrogen content for each of these vials was determined by weighing and multiplying by the stoichiometric mass ratio, which was taken to be 0.143711. The mass determination by weighing was done on a calibrated commercial scale that has an accuracy of ± 0.2 mg (0.03 mg hydrogen). The hydrogen content in the table is the sum of the polyethylene hydrogen and dextrose hydrogen. The uncertainty was taken to be 0.1 mg, our estimated uncertainty in the stoichiometry and sample purity.

The Bakelite cap contains hydrogen that is not uniformly distributed in the sample and that does not appear in the HTGR rods. To account for this characteristic we assign to these standards a parameter that is equal to 1.0

TABLE II
CALIBRATION STANDARDS FOR HYDROGEN MONITOR

Standard ID	H Contents (g)	Cap	Sample Height (cm)	^{235}U Contents (g)	Comments	Average Response	χ^2
1	0.5768	1.0	4.31	0.1036	CMB-1 LASL analytic chemistry samples encapsulated in polyethylene vials.	1.5004 ± 0.0012	28.10
2	0.6420	1.0	4.31	0.0920		1.5839 ± 0.0013	4.81
3	0.5713	1.0	4.31	0.1873		1.4991 ± 0.0012	1.36
4	0.6467	1.0	4.31	0.1916		1.5855 ± 0.0013	0.73
5	0.5696	1.0	4.31	0.2930		1.4972 ± 0.0012	1.25
6	0.6306	1.0	4.31	0.2782		1.5719 ± 0.0012	9.26
P-1	0.4396	0.0	5.00	0.0	Weighed poly-ethylene vials.	1.3115 ± 0.0011	0.06
P-2	0.5004	0.0	5.00	0.0		1.3712 ± 0.0011	0.07
P + Cap	0.4983	1.0	5.00	0.0	Encapsulation for CMB-1 standards	1.4238 ± 0.0014	16.19

when the cap is present and 0.0 when it is not. A sample of 10 randomly selected caps was weighed and found to have a relative standard deviation in mass of 0.87 . The uncertainty in this parameter was therefore assigned the value 1.0 . The height of the "2 dram" vials was about 5.0 cm with nominal contents of 450 mg H, and the fill height of the glass vials was 2.0 cm with nominal contents of 150 mg H. The fill height listed in the table is the weighted average for the encapsulated sample and is assigned an uncertainty of 0.1 cm.

Standards P-1 and P-2 are simply weighed polyethylene vials. Standard "P + Cap" is an empty glass vial with a cap and polyethylene encapsulation.

B. Experimental Procedure

Each standard of Table II was assayed three times over one continuous period and their responses were calculated as described above. Weighted averages for each response are listed in the table. A measure of the reproducibility of the system is $\chi^2/\text{degree of freedom}$ (χ^2/deg) for these averages. They ranged from a low of 0.10 to a high of 1.34 with a simple average of 0.71, giving confidence that the experimental variations were statistical.

C. Fitting of Data

Linear least squares fits were done to obtain best values for the parameters A_j , the associated variance-covariance matrix, and the value of χ^2/deg for each fit. Parameters that were considered to represent the characteristics of the samples were hydrogen content, fill height, baxelite cap, and ^{235}U content. Although not rigorously correct from a statistics point of view, a term for hydrogen-squared content was included as an independent parameter. Such a procedure is certainly not valid for situations where this term becomes comparable to or larger than the linear term but may be a reasonable way to include such effects if they are small perturbations on the response.

The responses of the first nine standards were the data to be fit, and the parameter sets were varied to see the effect on χ^2/deg , reasonableness of parameters, and resulting assay accuracy. Table III gives a list of parameter sets obtained with χ^2/deg less than 30. Trial assays were done with each of the sets to find overall uncertainties that result from their use. In order to have the assay uncertainties reflect the imperfect fit of the linear model to the calibration data, the variance-covariance matrix associated with each was multiplied by χ^2/deg . The assay uncertainties obtained for each of the sets is listed in Table III as ΔH . Two objections to using the set with the

TABLE III
HYDROGEN MONITOR CALIBRATION PARAMETERS

Set	χ^2/deg	A_1	$A_2(\text{H}, \text{g}^{-1})$	$A_3(\text{Cap})$	$A_4(\text{H}^2, \text{g}^{-2})$	$A_5(\text{Ht}, \text{cm}^{-1})$	$\Delta\text{H}(\text{mg})$
H8M309	16.3	0.818	1.114	0.047	--	--	3.4
H8M409	12.4	0.833	1.046	0.045	0.078	--	3.5
H8M509	6.2	0.719	1.078	0.049	0.103	0.019	4.2

smallest χ^2/deg arise. First, the sign of the coefficient of fill height is physically unreasonable. One experimentally observes the response of the instrument to decrease as the hydrogen is moved from its central, optimum position. Hence a decrease in response is expected as the height of the sample is increased, which would give a negative sign to the coefficient of fill height. A second problem is the increase in the assay uncertainty, probably caused by the addition of a quantity that has a relatively large variance itself. To reduce the height uncertainty much below its 1-mm level would involve careful consideration of the weighted averaging of polyethylene and dextrose heights. Finally, ignoring the height parameter biases the assay by, at most, 0.6%. For these reasons, the set H8M409 was chosen as representing the best parameters and variance-covariance matrix. The curve of Fig. 2 shows the hydrogen dependence of this set and the responses of the standards, corrected for the cap presence, that generated it.

V. UNKNOWN ASSAY AND ANALYSIS

To obtain the hydrogen content of the HTGR rods, they were assayed in the hydrogen monitor along with two standards for each blend. The sequence was chamber empty, first standard, four sequential rods, second standard. The standards associated with the various blends were blend 12--standards 2 and 4, blend 13--standards 2 and 4, and blend 14--standards 4 and 6. This procedure gave four to seven replicate assays of each standard for each day, permitting an assessment of system stability. Average responses, their uncertainties, and χ^2/deg for each standard were calculated for each continuous running

Fig. 2.
Calibration data and fitted curve for the hydrogen monitor response.

period. χ^2/deg greater than 2.0 occurred for 40% of the cases (5 to 10 would be expected on the basis of counting statistics). and for these the uncertainty of the average response was increased by a factor of $\sqrt{\chi^2/\text{deg}}$. Using as input the parameters and variance-covariance matrix of set H8M409, the average responses of the standards, and the response of each unknown, the hydrogen content of each of the latter was computed relative to the two standards. The constituents of the standards and their uncertainties are discussed in Sec. III. The constituents of the rods were taken to be $\text{Cap} = 0.0 \pm 0.01$, $H^2 = 0.400 \pm 0.010 \text{ g}^2$, and $\text{Height} = 5.00 \pm 0.100 \text{ cm}$.

Since the nominal H^2 value was valid only for total hydrogen contents of 0.6325 g, an analytic expression was used to correct the hydrogen with an H^2 correction based on the initial assay results. Several cases were run using an iterative procedure to arrive at self-consistent values of H and H^2 . These agreed with the analytically generated correction to better than 0.3 mg.

The values for hydrogen were the weighted averages of the two determinations relative to the standards. These differed from the values obtained relative to each standard by about 3 mg, which was also the statistical accuracy of the determination.

Because the uranium assay has different sensitivities to the hydrogen in the rod and in the encapsulation, these quantities were determined. The rod plus encapsulation masses were all determined to 0.1 mg by weighing with a calibrated commercial scale and the rod masses were supplied by NBL. The difference, the mass of the polyethylene encapsulation, was divided by the stoichiometric ratio for hydrogen in polyethylene to obtain encapsulation hydrogen. The difference between this quantity and the H monitor assay results is the rod hydrogen mass. The average values and relative standard deviation for the 48 rods in each batch are: Batch 12--171.5 $\pm$ 2.7 mg (1.6%), Batch 13--162.7 $\pm$ 3.5 mg (2.1%), and Batch 14--160.0 $\pm$ 5.3 mg (3.3%). These spreads are large enough to justify the use of the assay results for each rod in the correction for the forthcoming ^{235}U assay.

VI. RESULTS AND CONCLUSIONS

The hydrogen monitor has been calibrated for measurements in the vicinity of 600-mg hydrogen. With the current calibration and standards, the estimated accuracy is ± 4.5 mg, which is based on the difference in assay results for the same unknown for two different standards and measurement precisions. Before proceeding with work that improves the precision of the monitor, more work will need to be done to remove this ± 3 -mg discrepancy. Likely candidates for investigation are the exact form of the response, which is likely to be more complex than the simple linear response assumed here, and use of calibration standards, which more closely match the rods (perhaps by elimination of the Bakelite cap).

The assay results are tabulated in Table IV. A comparison of the average values for each batch, recorded in Sec. V and those values in Table I show the assay values to be 15 to 30% higher than the preliminary estimates.

TABLE IV
MASS OF HYDROGEN IN GRAMS

ID	Total	Rods	Poly	ID	Total	Rods	Poly	ID	Total	Rods	Poly
1248	0.6335	0.1691	0.4644	1348	0.6314	0.1710	0.4604	1448	0.6342	0.1626	0.4716
1247	0.6327	0.1715	0.4612	1347	0.6118	0.1605	0.4513	1447	0.6237	0.1558	0.4679
1246	0.6283	0.1712	0.4571	1346	0.6231	0.1622	0.4609	1446	0.6060	0.1553	0.4507
1245	0.6337	0.1749	0.4588	1345	0.6378	0.1663	0.4715	1445	0.6253	0.1631	0.4622
1244	0.6397	0.1699	0.4698	1344	0.6279	0.1618	0.4661	1444	0.6412	0.1622	0.4790
1243	0.6432	0.1709	0.4723	1343	0.6156	0.1633	0.4523	1443	0.6276	0.1617	0.4659
1242	0.6484	0.1717	0.4767	1342	0.6311	0.1655	0.4656	1442	0.6163	0.1557	0.4606
1241	0.6560	0.1750	0.4810	1341	0.6329	0.1611	0.4718	1441	0.6379	0.1546	0.4833
1240	0.6478	0.1719	0.4759	1340	0.6299	0.1649	0.4650	1440	0.6097	0.1578	0.4519
1239	0.6439	0.1699	0.4840	1339	0.6339	0.1645	0.4694	1439	0.6266	0.1592	0.4674
1238	0.6430	0.1727	0.4703	1338	0.6369	0.1645	0.4724	1438	0.6402	0.1561	0.4841
1237	0.6488	0.1704	0.4784	1337	0.6222	0.1604	0.4618	1437	0.6181	0.1473	0.4708
1236	0.6362	0.1738	0.4624	1336	0.6272	0.1621	0.4651	1436	0.6181	0.1689	0.4492
1235	0.6464	0.1739	0.4725	1335	0.6228	0.1609	0.4619	1435	0.6152	0.1545	0.4607
1234	0.6320	0.1693	0.4627	1334	0.6253	0.1653	0.4600	1434	0.6270	0.1533	0.4737
1233	0.6489	0.1711	0.4778	1333	0.6386	0.1687	0.4699	1433	0.6054	0.1507	0.4547
1232	0.6189	0.1695	0.4494	1332	0.6419	0.1656	0.4763	1432	0.6342	0.1643	0.4699
1231	0.6347	0.1767	0.4580	1331	0.6432	0.1628	0.4804	1431	0.6107	0.1609	0.4498
1230	0.6496	0.1707	0.4789	1330	0.6379	0.1615	0.4764	1430	0.6261	0.1658	0.4603
1229	0.6324	0.1664	0.4660	1329	0.6100	0.1592	0.4508	1429	0.6437	0.1613	0.4814
1228	0.6496	0.1682	0.4814	1328	0.6267	0.1640	0.4627	1428	0.6340	0.1613	0.4727
1227	0.6388	0.1690	0.4698	1327	0.6063	0.1550	0.4513	1427	0.6334	0.1605	0.4729
1226	0.6305	0.1692	0.4613	1326	0.6312	0.1612	0.4700	1426	0.6359	0.1648	0.4711
1225	0.6453	0.1697	0.4756	1325	0.6459	0.1607	0.4852	1425	0.6263	0.1641	0.4622
1224	0.6324	0.1663	0.4661	1324	0.6297	0.1593	0.4704	1424	0.6365	0.1687	0.4678
1223	0.6208	0.1712	0.4496	1323	0.6255	0.1592	0.4663	1423	0.6285	0.1629	0.4656
1222	0.6242	0.1703	0.4539	1322	0.6204	0.1635	0.4569	1422	0.6209	0.1614	0.4595
1221	0.6365	0.1727	0.4638	1321	0.6234	0.1648	0.4586	1421	0.6404	0.1616	0.4788
1220	0.6313	0.1733	0.4580	1320	0.6349	0.1632	0.4717	1420	0.6227	0.1619	0.4608
1219	0.6231	0.1726	0.4505	1319	0.6462	0.1653	0.4809	1419	0.6233	0.1629	0.4604
1218	0.6412	0.1705	0.4707	1318	0.6326	0.1653	0.4673	1418	0.6263	0.1583	0.4680
1217	0.6498	0.1695	0.4803	1317	0.6341	0.1655	0.4686	1417	0.6344	0.1590	0.4754
1216	0.6246	0.1714	0.4532	1316	0.6514	0.1653	0.4861	1416	0.6349	0.1652	0.4697
1215	0.6409	0.1708	0.4701	1315	0.6153	0.1629	0.4524	1415	0.6338	0.1647	0.4691
1214	0.6359	0.1712	0.4647	1314	0.6376	0.1665	0.4711	1414	0.6315	0.1674	0.4641
1213	0.6487	0.1709	0.4778	1313	0.6436	0.1684	0.4752	1413	0.6304	0.1622	0.4682
1212	0.6463	0.1669	0.4794	1312	0.6227	0.1653	0.4574	1412	0.6419	0.1688	0.4731
1211	0.6340	0.1694	0.4646	1311	0.6477	0.1664	0.4813	1411	0.6327	0.1713	0.4614
1210	0.6513	0.1739	0.4774	1310	0.6293	0.1621	0.4672	1410	0.6397	0.1601	0.4796
1209	0.6216	0.1711	0.4505	1309	0.6098	0.1584	0.4514	1409	0.6243	0.1571	0.4672
1208	0.6413	0.1745	0.4668	1308	0.6416	0.1644	0.4772	1408	0.6144	0.1629	0.4515
1207	0.6451	0.1845	0.4606	1307	0.6391	0.1596	0.4795	1407	0.6234	0.1560	0.4674
1206	0.6388	0.1682	0.4706	1306	0.6320	0.1626	0.4694	1406	0.6206	0.1562	0.4644
1205	0.6330	0.1710	0.4620	1305	0.6115	0.1573	0.4542	1405	0.6223	0.1585	0.4638
1204	0.6482	0.1704	0.4778	1304	0.6257	0.1593	0.4664	1404	0.6393	0.1615	0.4778
1203	0.6485	0.1656	0.4829	1303	0.6240	0.1590	0.4650	1403	0.6291	0.1594	0.4697
1202	0.6471	0.1662	0.4809	1302	0.6253	0.1632	0.4621	1402	0.6465	0.1637	0.4828
1201	0.6320	0.1699	0.4621	1301	0.6109	0.1595	0.4514	1401	0.6433	0.1599	0.4834

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