

# **CSSX Radiolytic H<sub>2</sub> Generation ("Thermolysis") Final Report**

Bruce Mincher

January 2009



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**January 2009**

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## Aqueous Separations and Radiochemistry

# CSSX Radiolytic H<sub>2</sub> Generation ("Thermolysis") Final Report

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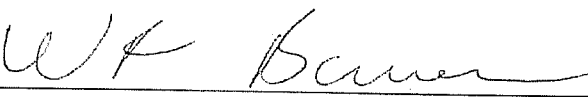
  
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## ABSTRACT

The purpose of this work was to determine the radiolytic hydrogen gas yield of irradiated Caustic Side Solvent Extraction(CSSX) solvent at several temperatures. The active ingredient of this solvent is calix[4]arene-bis-(*t*-octylbenzo) crown-6, a calixarene crown ether used for cesium complexation. The solvent also contains 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol, a fluorinated alcoholic solvent modifier used to improve the solubility of the calixarene and its cesium complex in the Isopar L diluent. Isopar L is a branch-chain alkane and comprises most of the mixture. Samples of this solution were irradiated to various absorbed  $\gamma$ -ray doses in gas-tight sample containers over the temperature range 18-48°C, which were then sampled for hydrogen gas content. The G-value for hydrogen production did not vary with temperature. The yields were found to be 0.091  $\mu\text{mol J}^{-1}$  at 48°C, 0.093  $\mu\text{mol J}^{-1}$  at 28°C and 0.095  $\mu\text{mol J}^{-1}$  at 18°C. The mean value is  $0.093 \pm 0.002$   $\mu\text{mol J}^{-1}$  (2% RSD). The methods are described below.





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## ACRONYMS

CSSX	Caustic Side Solvent Extraction
FWT	Far West Technology
GC	gas chromatography
OD	optical density
PLOT	Porous Layer Open Tubular
SWPF	Salt Waste Processing Facility
TCD	thermal conductivity detector
VOA	Volatile Organics Analysis



# **CSSX Radiolytic H<sub>2</sub> Generation (“Thermolysis”) Final Report**

## **1. EXPERIMENTAL METHODS**

### **1.1 Preparation of Solvent**

Approximately 500 mL of “water-saturated” Caustic Side Solvent Extraction (CSSX) solvent was supplied to INL by Parsons/ Salt Waste Processing Facility (SWPF) project. This solvent was further equilibrated with water prior to irradiation by vigorously mixing the solvent with an equal volume of 18-mega-ohm (Mohm) water, prepared using an ion exchange purification system, for 5 minutes. This was allowed to settle for 5 minutes, after which the organic phase was separated. An additional 1 microliter (μL) of pure water was added to each 50 milliliter (mL) of water-saturated solvent [Leugemors 2008]. Each irradiated sample consisted of 10.0 mL of this water-saturated solvent loaded into a 25-mL stainless steel, swagelok sample cylinder.

### **1.2 Sample Containers**

The original procedure specified that the samples would be irradiated in standard 40-mL septum-sealed Volatile Organics Analysis (VOA) vials. These are glass vials, sealed with septum screw-caps and are commonly used for headspace gas sampling. However, during preliminary work with hydrogen gas standards it was found that no available septum type prevented loss of hydrogen during storage. Therefore, the samples were irradiated in 25-mL stainless steel sample containers (Swagelok SS4CS TW-25) fitted with SS 6P6T valves. An additional Swagelok fitting on the valve allowed use of a septum for gas sampling. These Swagelok containers were found to be suitable only for single-irradiation-use. When used containers were re-filled with calibration gas, the resulting hydrogen analytical value for this gas was as much as 40% low. Multiple uses of unirradiated containers did not exhibit this problem. The cause may be radiolytic embrittlement of valve packing, resulting in a sample valve that leaks once it is operated following the irradiation. However, the cause was not pursued as it was outside the scope and budget of this project. A single-irradiation-use policy was instituted. As shown by irradiated hydrogen calibration gas samples, and standard trip blank analyses this policy prevented anomalously low hydrogen determinations.

### **1.3 Sample Irradiations**

Samples were irradiated with <sup>60</sup>Co γ-rays using a Nordion 220E Gammacell (Nordion, Ottawa, Ontario, Canada). Each temperature/absorbed dose condition was irradiated in triplicate. The duration of the irradiation was selected using the automated timers on the irradiator control panel, to achieve selected absorbed doses (Gammacell 2003). The center-line, base-plate absorbed dose in the irradiator sample chamber is currently 10 kGy h<sup>-1</sup> (1.0 MRad h<sup>-1</sup>), based on Fricke dosimetry (Klassen et al. 1999). However, the actual dose rate experienced by a given sample varies with its exact position in the sample chamber (Gammacell 2003). At 2-3 inches above the base plate, the absorbed dose is as much as 40% higher. Therefore, each sample was accompanied by its own Far West Technology (FWT)-60 radiochromic film dosimetry (FWT Technology, Goleta, CA, USA). Two to four films were contained in a paper envelope taped to the sample container. The film changes color with absorbed dose, and the optical density (OD) of the films was read with a film reader supplied by the vendor. The film OD was calibrated by reference to the center-line dose rate as determined by Fricke dosimetry. This calibration curve is: Dose (kGy) = 180.6OD<sup>2</sup> + 18.51OD + 2.32, R = 0.977. Duplicate or triplicate films were

attached to each sample container and the average OD was used to calculate the absorbed dose, which is reported here in MRad  $\pm 1\sigma$ . The average error, based on replicate determinations and expressed as a relative standard deviation for absorbed dose measurements was 2.2%.

The effect of the steel containers upon measured dose was also evaluated. The neck was cut off of one container so that dosimetry could be placed inside and outside on opposite sides of the same wall. This was then irradiated to provide optical densities in the range of the dosimetry. The outside dosimeters developed an OD =  $0.225 \pm 0.005$  (N=5) (1.56 MRad) and the inside dosimeters developed an optical density of  $0.224 \pm 0.004$  (N=3) (1.55 MRad). It was concluded that the absorbed dose delivered to the sample is identical to that measured by the radiochromic films attached to the outside of the containers.

The temperature during irradiation was determined with a calibrated thermocouple, inserted into the center of the sample chamber with an accuracy of  $\pm 1^\circ\text{C}$ . The ambient temperature in the empty irradiator sample chamber due to gamma heating of the shielding is currently  $46.0 \pm 1^\circ\text{C}$ .

## 1.4 Hydrogen Gas Analysis

Hydrogen gas in sample headspace was determined by gas chromatography (GC), with a Molecular Sieve 5Å Porous Layer Open Tubular (PLOT) column and a thermal conductivity detector (TCD). The injector and detector were maintained at  $50^\circ\text{C}$ . Argon was used as the mobile phase to maximize sensitivity for hydrogen. Temperature and flow rates were optimized to assure baseline resolution between hydrogen and oxygen, at  $30^\circ\text{C}$  and head pressure set at 8 psi, respectively. Injection volumes and syringe sizes were  $100\mu\text{L}$ . Standard gas was certified with analytical accuracy of  $\pm 0.02\%$  and acquired from Scott Specialty Gases. Blanks consisted of gas mix containing 1.4% hydrogen.

Standard calibration gas was also used to fill sample containers and was irradiated to an absorbed dose as high as that received by any sample and reanalyzed to ensure that irradiation did not affect the result. Finally, sample containers with calibration gas that were not irradiated accompanied each CSSX sample set as a “trip blank”. Each sample was analyzed in duplicate and the results are presented as  $\%H_2 \pm 1\sigma$ . Raw data, including calibration data and in-lab calibration gas checks are available as electronic files. The average error, based on replicate determinations and expressed as a relative standard deviation was 1.5%.

## 1.5 Modifications to Original Procedure

The use of the steel containers required a number of changes to the originally envisioned procedure. Their larger size precluded the sequence of steps dependent on initiating the irradiation of all nine samples in a given batch simultaneously. Further, when even three containers were irradiated simultaneously, gamma heating of the steel caused temperature control issues. The irradiator sample chamber ambient temperature is approximately  $46\text{--}48^\circ\text{C}$ . For the nominal  $48^\circ\text{C}$  temperature samples, the nominal 4-MRad and 10-MRad sample irradiations were initiated simultaneously. The nominal 4-MRad samples were removed after four hours exposure, and the nominal 10-MRad samples were removed after an additional 6 hours. This resulted in an unanticipated temperature fluctuation of approximately  $6^\circ\text{C}$  for the ambient temperature 10-MRad samples, due to gamma heating. These irradiations therefore varied over an  $8^\circ\text{C}$  range for all samples. The nominal 32-MRad samples were irradiated separately, in three shifts for dosimetry purposes. This was due to the latter absorbed dose exceeding the range of the radiochromic film dosimetry. Thus, these samples were irradiated in the sequence of three timed exposures, each with separate dosimetry to achieve the desired total absorbed dose, without exceeding the range of the films. The sum of the three dosimetry results was used to give the total absorbed dose, as envisioned in the original procedure.

For cooled samples, the off-gas of a liquid nitrogen dewar was used to decrease the temperature in the sample chamber. Samples were irradiated individually or in pairs as necessary to achieve proper cooling and absorbed dose targets. Constant temperature was achieved by adjusting the dewar pressure boost valve until the dewar pressure was slightly above the set point for its relief valve. The slow leak through the relief valve maintained a constant dewar internal pressure, thus constant gas flow through the cooling line to maintain constant temperature inside the sample chamber. Fine adjustments were made with a throttle valve on the gas line. The temperature of nitrogen-cooled samples was readily maintained at  $\pm 2^{\circ}\text{C}$ . The arrangement is shown in Figure 1.



Figure 1. Configuration of cooled irradiation system. Liquid nitrogen supply is on the left, with flex line for cold gas delivery shown inserted into irradiator sample chamber (right), in the irradiate position. Thermocouple readout is shown on top of sample chamber. On the table in the background is the FWT dosimetry reader.



## 2. RESULTS

Preliminary irradiations of 1% H<sub>2</sub> calibration gas were conducted in the stainless sample containers. Two containers were filled with calibration gas on 8/25/08 and irradiated on 8/27/08–8/28/08. These were analyzed on 9/2/08. The results are shown in Table 1. It can be seen that the irradiation did not affect the concentration of H<sub>2</sub> measured in the calibration gas.

Table 1. Preliminary calibration gas irradiation results.

ID	Sample	Absorbed Dose (MRad)	H <sub>2</sub> (%)	T (°C)
082708-1IB	1.0% H <sub>2</sub>	36	1.05	45.6
082708-2IB	1.0% H <sub>2</sub>	36	1.05	45.6

### 2.1 Nominal 48°C Irradiations

The nominal 4-MRad and 10-MRad ambient temperature samples were prepared on 09/30/08, irradiated on 9/30/08 and analyzed on 10/08/08. A trip blank, and irradiated calibration gas were prepared on 10/02/08, irradiated on 10/02/08–10/03/08 and re-analyzed on 10/08/08. The nominal 32-MRad samples were prepared on 10/14/08, irradiated on 10/14/08–10/15/08 and analyzed on 10/16/08. Two trip blanks accompanied the 32-MRad samples. One was freshly prepared on 10/02/08 and one on 10/14/08. Both were found to contain hydrogen gas concentration within the analytical uncertainty, demonstrating that the containers are capable of holding hydrogen for at least 14 days. The analytical results for these samples are shown in Table 2.

Table 2. Nominal temperature (48°C) irradiation results.

ID	Sample	Absorbed Dose (MRad)	H <sub>2</sub> (%)	T (°C)
100208TB	1.1% H <sub>2</sub>	NA	1.1	NA
100208IB	1.1% H <sub>2</sub>	36	1.2	46
093008-1	CSSX	4.04±0.04	4.7±0.1	54.2
093008-2	CSSX	3.96±0.04	4.9±0.2	54.2
093008-3	CSSX	3.25±0.01	5.4±0.1	54.2
093008-4	CSSX	9.68±0.24	12.5±0.5	48.2-54.2
093008-5	CSSX	11.1±0.35	14.3±0.1	48.2-54.2
093008-6	CSSX	11.8±0.22	14.8±0.4	48.2-54.2
100508TB	1.3% H <sub>2</sub>	NA	1.3	NA
101408TB	1.3% H <sub>2</sub>	NA	1.3	NA
101408-1	CSSX	37.0±0.99	32.0±0.4	48.2
101408-2	CSSX	30.9±1.64	29.8±0.6	48.2
101408-3	CSSX	31.9±0.71	30.8±0.1	48.2

NA indicates not irradiated

## 2.2 Nominal 28°C Irradiation

Six samples were prepared on 10/16/08. These were the first samples to be irradiated with nitrogen cooling. Initial attempts to irradiate the nominal 4-MRad samples were problematic due to the LN<sub>2</sub> dewar being of insufficient capacity. All three of these samples received 30-minutes irradiation at  $28 \pm 2^\circ\text{C}$  on 10/20/08. Sample 101608-1 then received an additional 30 minutes on 10/22/08, then 90 minutes on 10/27/08 and 90 minutes on 10/28/08. A larger capacity dewar was procured by 10/28/08. Sample 101608-2 then received an additional 3 hrs 30 minutes on 10/28/08. Sample 101608-4 received 9 hrs and 30 minutes on 10/29/08. Samples 101608-3 received 3 hrs 30 minutes on 10/30/08. These samples were analyzed on 11/06/08. Sample 101608-5 received 6 hours on 12/01/08 and 4 hours on 12/02/08 for a total of ten hours irradiation. Sample 101608-6 received five hours on 12/02/08 and 5 hours on 12/03/08 for a total of ten hours. These were analyzed on 12/04/08.

The samples 120308-1 through 120308-3 and a trip blank 120408TB were prepared on 12/04/08. Samples 120308-1 and 120408-2 received 12 hours on 12/08/08, and an additional 10 hours on 12/09/08 for a total of 22 hours. Sample 120308-3 was irradiated for 12 hours on 12/10/08, 5.5 hours on 12/15/08 and 9 hours on 12/16/08. Samples 120308 1 and 2 were analyzed on 12/12/08. Sample 120308-3 and the trip blank were analyzed 12/23/08. The trip blank results show that hydrogen storage in the sample containers for up to 19 days did not affect the analytical results.

Table 3. Nominal 28°C irradiation results.

ID	Sample	Absorbed Dose (MRad)	H <sub>2</sub> (%)	T (°C)
101608-1	CSSX	5.02±0.07	8.0	28±2
101608-2	CSSX	4.78±0.06	7.5±0	28±2
101608-3	CSSX	3.34±0.12	6.9±0.14	28±2
101608-4	CSSX	13.2±0.07	15.7±0.21	28±2
101608-5	CSSX	11.2±0.01	17.2±0.57	28±2
101608-6	CSSX	10.1±0.01	17.5±0.07	28±2
120308-1	CSSX	22.0±0.34	27.8±1.34	28±2
120308-2	CSSX	17.1±0.49	27.9±0.57	28±2
120308-3	CSSX	39.9±0.46	34.8±0.14	28±2
120408TB	1.2% H <sub>2</sub>	NA	1.2	NA

NA indicates not irradiated

## 2.3 Nominal 18°C Irradiations

Six of nine samples (121108-1-6) were prepared on 12/10/08. Samples 121108-1 and -2 were irradiated for four hours on 12/17/08. Sample 121108-3 was irradiated for four hours on 12/18/08. Sample 121108-4 was irradiated for ten hours on 12/18/08. Samples 121108-5, 6 were irradiated for seven hours on 12/22/08, and another three hours on 1/5/09. Samples 122308 1-3 were prepared on 12/23/08. Samples 122308 1-2 were irradiated for 9 hours on 1/6/09, on 1/7/09 for 10 hours and another 10 hours on 1/12/09. Sample 122308-3 was irradiated for 10 hours on 1/13/09, 11 hours on 1/14/09 and 10 hours on 1/15/09. They were analyzed on 1/19/09. A trip blank was prepared on 12/23/09 and also analyzed on 1/19/09, demonstrating that and storage for up to 27 days had little effect on H<sub>2</sub> analytical results.

Table 4. Nominal 18°C irradiation results.

ID	Sample	Absorbed Dose (MRad)	H <sub>2</sub> (%)	T (°C)
121108-1	CSSX	3.8±0.61	6.0±0.0	18±2
121108-2	CSSX	3.4±0.05	6.6±0.0	18±2
121108-3	CSSX	3.1±0.05	6.2±0.0	18±2
121108-4	CSSX	10.8±0.09	15.8±0.14	18±2
121108-5	CSSX	9.2±0.11	15.3±0.07	18±2
121108-6	CSSX	11.4±0.22	14.0±0.42	18±2
122308-1	CSSX	26.5±0.43	32.0±0.21	18±2
122308-2	CSSX	26.1±0.31	32.2±0.35	18±2
122308-3	CSSX	31.3±0.53	33.7±0.42	18±2
122308TB	1.2% H <sub>2</sub>	NA	1.0	NA
NA indicates not irradiated				

### 3. DISCUSSION

The  $G$ -values, or hydrogen yields ( $\mu\text{mol J}^{-1}$ ) for irradiated CSSX samples at various temperatures were calculated based on the data given in Tables 2-4. It should be noted that older literature used units for  $G$ -values of molecules  $100 \text{ ev}^{-1}$ . The proper unit  $\mu\text{mol J}^{-1}$  is converted to the archaic unit molecules  $100 \text{ ev}^{-1}$  by multiplying by 10. The  $\%H_2$  values in the tables were converted to  $\mu\text{mol H}_2$  based on the ideal gas law:

$$PV = nRT, \text{ where:}$$

$$P = 1 \text{ atm}$$

$$V = \%H \times 0.015 \text{ L headspace}$$

$$R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$T = 294\text{K}$$

$$1 \text{ mol} = 1 \times 10^6 \mu\text{mol}$$

The result in  $\mu\text{mol H}_2$  was then divided by the mass of CSSX solvent irradiated, which is 0.010 L ( $0.86 \text{ kg L}^{-1}$ ) =  $8.6 \times 10^{-3} \text{ kg}$ . The resulting value, in  $\mu\text{mol kg}^{-1}$ , was plotted versus the absorbed dose in Gy ( $\text{J kg}^{-1}$ ), and is shown in Figure 2. The slopes of the linear portion of these curves provide the initial  $G$ -values or hydrogen yields at each temperature, which are shown in Figure 3. The raw data used to plot Figure 2 is given in Table 5.

Table 5. Radiolytically produced  $H_2$  and absorbed dose for samples at all temperatures.

ID	$H_2$ ( $\mu\text{mol kg}^{-1}$ )	Absorbed Dose ( $\text{J kg}^{-1}$ )
093008-1	3396	40,400
093008-2	3541	39,600
093008-3	3902	32,500
093008-4	9033	96,800
093008-5	10,333	110,100
093008-6	10,695	118,100
101408-1	23,123	370,000
101408-2	21,534	309,000
101408-3	22,256	319,000
101608-1	5781	50,200
101608-2	5420	47,800
101608-3	4986	33,400
101608-4	11,345	132,000
101608-5	12,492	112,000
101608-6	12,646	101,000
120308-1	20,088	220,000
120308-2	20,161	171,000
120308-3	25,147	399,000

Table 5. (continued).

ID	H <sub>2</sub> ( $\mu\text{mol kg}^{-1}$ )	Absorbed Dose (J kg <sup>-1</sup> )
121108-1	4336	38,000
121108-2	4769	34,000
121108-3	4480	31,000
121108-4	11,417	108,000
121108-5	10,056	92,000
121108-6	10,117	114,000
122308-1	19,149	265,000
122308-2	18,860	261,000
122308-3	22,618	313,000

It can be seen upon visual inspection of Figure 2 that all data lie on the same curve, meaning that the H<sub>2</sub> yield for all temperatures is the same, within analytical uncertainty. Using the linear portion of the data as shown in Figure 3, from the origin to the nominal 10 kGy samples, the yields are found to be 0.091  $\mu\text{mol J}^{-1}$  at 48°C, 0.093  $\mu\text{mol J}^{-1}$  at 28°C and 0.095  $\mu\text{mol J}^{-1}$  at 18°C. The mean value is  $0.093 \pm 0.002 \mu\text{mol J}^{-1}$  (2% RSD). This yield is slightly higher than values tabulated for liquid phase alkanes of 0.02-0.06  $\mu\text{mol J}^{-1}$  (Spinks and Woods 1973).

Also upon inspection of Figure 3 it can be seen that the two data points corresponding to 28°C (nominal 30 MRad) samples 120308-1 and 2 appear to have slightly higher hydrogen yields than expected. This is probably due to an anomalously low absorbed dose measurement. It was found that the color developed in the radiochromic film dosimeters is different in the nitrogen atmosphere created by sample cooling (see lab notebook, page 14) than in air. It was subsequently found that when the films were allowed to stand in air for a few hours after irradiation, the normal color developed. All future samples were allowed to develop the proper color before reading.

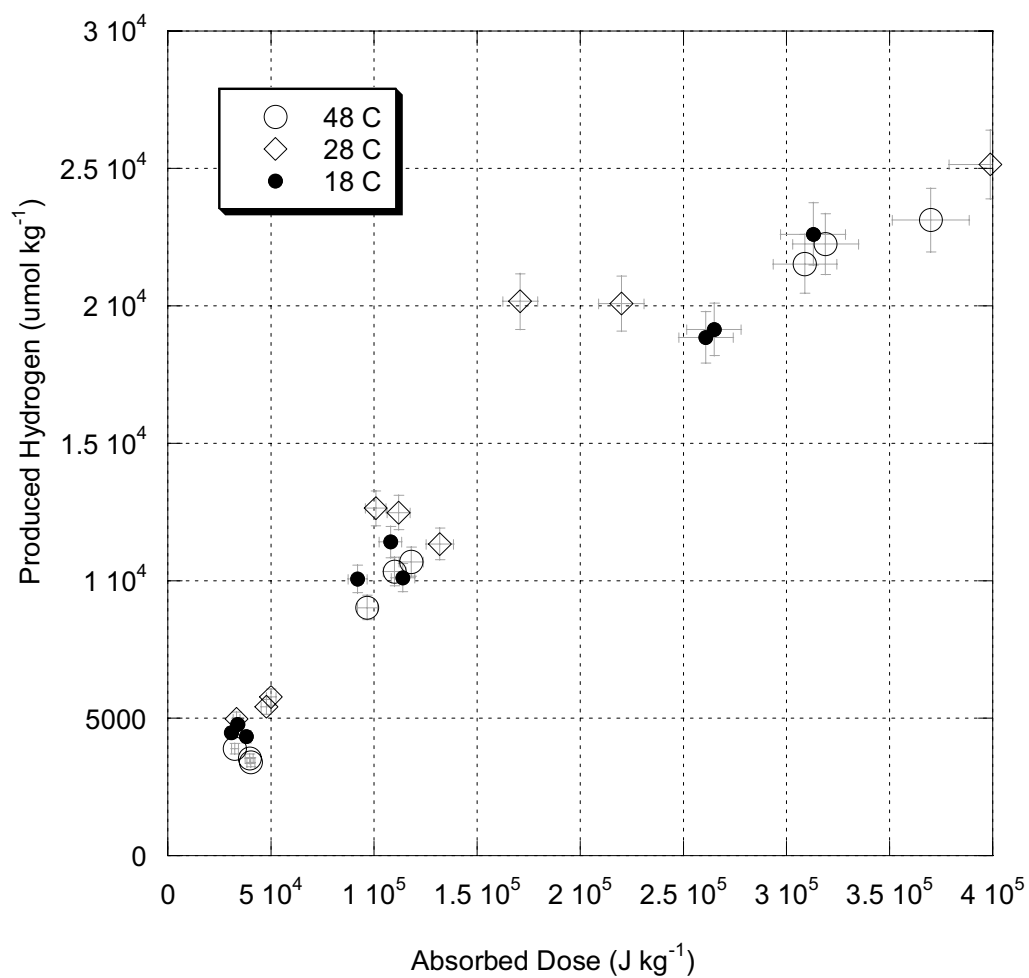


Figure 2. Hydrogen yield as a function of absorbed dose for water saturated CSSX solvent samples irradiated at various temperatures. Error bars shown are randomly assigned at  $\pm 5\%$ . Actual errors are lower, as described in the text.

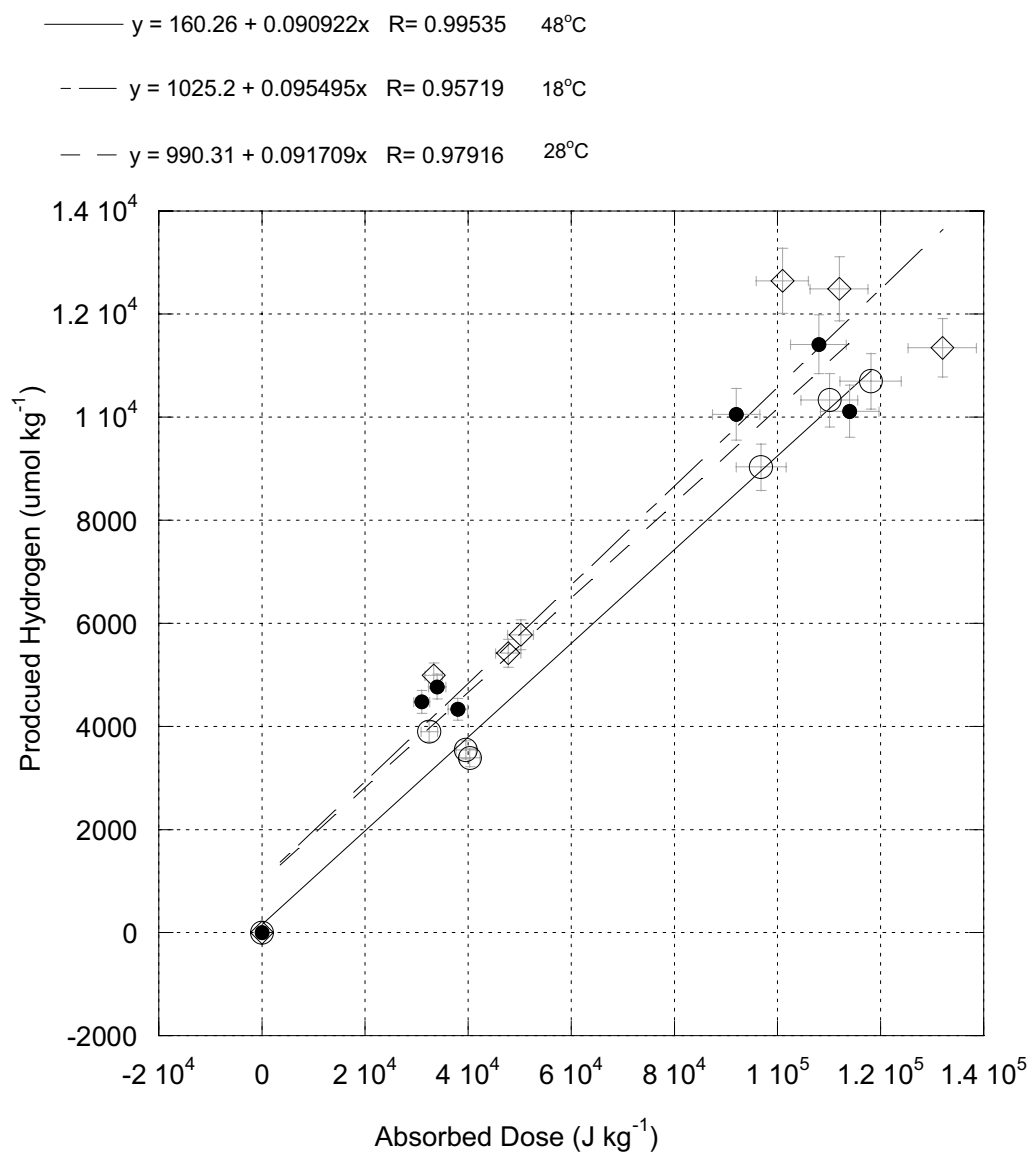


Figure 3. Initial  $G$ -values for the production of  $\text{H}_2$  during  $\gamma$ -irradiation of water saturated CSSX solvent. Error bars shown are randomly assigned at  $\pm 5\%$ . Actual errors are lower, as described in the text.

## 4. CONCLUSIONS

The change in temperature over the range 18°C – 48°C had no measurable effect on the H<sub>2</sub> yield for irradiated water-saturated CSSX solvent. That yield was  $0.093 \pm 0.002 \mu\text{mol J}^{-1}$  (0.93 molecules 100 eV<sup>-1</sup>).



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## **Appendix 1**

### **Thermolysis Testing Procedure Salt Waste Processing Facility CSSX Solvent**

# Appendix 1

## Thermolysis Testing Procedure. Salt Waste Processing Facility CSSX Solvent

### Part 1.

Irradiation of known hydrogen samples and trip blanks to determine suitability of test method for retention and measurement of radiolytically generated hydrogen:

1. Prepare swagelok sample containers containing a known hydrogen concentration by filling with a calibration gas, at the analytical laboratory.
2. Irradiate known hydrogen samples in sample chamber for ~30 hours (equivalent to ~30 MRad absorbed dose).
3. Record the start time on the logsheet (Appendix B).
4. Record the irradiator sample temperature on the logsheet (Appendix B).
5. Upon completion record the stop time on the logsheet (Appendix B).
6. Maintain a subset of known hydrogen samples as trip blanks, to accompany samples to be irradiated.
7. Transfer the samples and trip blanks from the irradiator to the analytical laboratory.

### Part 2.

Irradiation of actual samples:

**NOTE:** *CSSX solvent will be saturated with 18-Mohm water by shaking equal volumes in a glass, separatory funnel prior to use in these experiments.*

1. Prepare desired number of 10 mL samples of CSSX water saturated solvent in 25 mL Swagelok sample containers for irradiation.
2. Attach radiochromic film dosimeters (hereafter called “dosimeters”) in triplicate to each vial in Step 1 above, by placing the films in a paper envelope taped to the vial.
3. Record the pre-irradiation sample chamber temperature indicated on the sample chamber thermocouple on the log sheet (Appendix B)
4. Place the samples above in the  $^{60}\text{Co}$  irradiator sample chamber.
5. Set the irradiator timer to achieve an approximate absorbed dose of 4 MRad.
6. Initiate the irradiation by pressing the START button on the irradiator control panel.
7. Record the irradiation start time and date on the log sheet (Appendix B).
8. Upon completion, remove the 4 MRad samples from the sample chamber.
9. Record the irradiation stop time and date on the log sheet (Appendix B).
10. Read the optical absorbance of the neutral density filter standards associated with the FWT60 radiochromic film reader, and log the results daily on the log sheet (Appendix B), when dosimetry is in progress.
11. Read the optical absorbance of the radiochromic film dosimeters for the 4 MRad samples using the FWT60 radiochromic film reader. Log the results on the logsheet (Appendix B).

12. Set the irradiator timer to achieve an approximate absorbed dose of 10 MRad.
13. Initiate the irradiation for the nominal 10-MRad samples by pressing the START button.
14. Record the irradiation start time and date on the log sheet (Appendix B).
15. Upon completion, remove the 10 MRad samples from the sample chamber.
16. Record the irradiation stop time and date on the log sheet (Appendix B).
17. Read the optical absorbance of the radiochromic film dosimeters for the 10 MRad samples using the FWT60 radiochromic film reader. Log the results on the logsheet (Appendix B).

**NOTE:** *The duration of the remaining sample irradiations is above the range of the radiochromic films. Sequential additive irradiations with multiple dosimeters are necessary. Record the results for each dosimeter on the logsheet at the end of each irradiation. (Appendix B). The sum gives the dose for the entire nominal 32 MRad irradiation.*

18. Set the irradiator timer for 10-12 hours.
19. Initiate the irradiation for the initial stage of the 32 MRad irradiation by pressing the START button.
20. Record the irradiation start time and date on the log sheet (Appendix B).
21. Upon completion of the irradiation in step 19 remove and read the radiochromic film dosimeters from the 32 MRad samples. Record the results on the logsheet (Appendix B). Attach new dosimeters to the samples.
22. Record the irradiation stop time and date on the logsheet (Appendix B).
23. Set the irradiator timer to 10-12 hours.
24. Re-initiate the irradiation for the required remaining duration by pressing the START button.
25. Record the irradiation start time and date on the log sheet (Appendix B).
26. Upon completion remove and read the radiochromic film dosimeters for the 32 MRad samples. Record the results on the logsheet (Appendix B). Attach new dosimeters to the samples.
27. Set the timer for the remaining duration necessary to achieve approximately 32 MRads total.
28. Press the START button.
29. Upon completion remove the samples and read the film dosimeters.
30. Record the post-irradiation sample chamber temperature on the logsheet (Appendix B).
31. Transfer the samples and blanks to the analytical laboratory.
32. Ensure that the oxygen monitor for the irradiator room is in service.
33. Establish liquid nitrogen off-gas flow to the irradiator test chamber.
34. Adjust flow as necessary to achieve the desired sample chamber temperature of approximately 18°C. Record the pre-irradiation sample chamber temperature on the logsheet (Appendix B).
35. Repeat Steps 1-31 above.
36. Repeat Steps 32-33 above for a temperature of approximately 28°C. Then repeat Steps 1-31.

### Part 3. Hydrogen analysis:

**NOTE:** *Determination of  $H_2$  will be via gas chromatography (GC), with a Molecular Sieve 5Å Porous Layer Open Tubular (PLOT) column and a thermal conductivity detector (TCD). The injector and detector will be maintained at an elevated temperature, nominally 180°C. Nitrogen will be used as the mobile phase to maximize sensitivity for hydrogen. Temperature and flowrates will be optimized to assure baseline resolution between hydrogen and oxygen, nominally 30°C and 25 cm/sec, respectively. Injection volumes and syringe sizes will be selected to achieve the desired detection limits. Standard gases will be certified and acquired from qualified vendors. Blanks will consist of ambient air. Analyses will be performed following the generalized flowchart shown below, as appropriate.*

1. Pierce the sample container septum with the gas sampling syringe.
2. Opening the syringe valve and pull a volume of gas that is at least 2x the GC injection volume into the gas sampling syringe.
3. Close the syringe valve.
4. Depress the syringe plunger, then open and close the syringe valve to flush the syringe.
5. Repeat Steps 1-4.
6. Repeat Steps 1-3.
7. Depress the syringe plunger to the desired injection volume.
8. Open the syringe valve just prior to plunging the needle through the septum of the GC injection port.
9. Depress the syringe plunger to expel the injection volume into the injection port.
10. Initiate the GC temperature program.

Checked by:

William F. Bauer, Dept. Manager, Analytical Lab

Date

Approved by:

Jack D. Law, Dept. Manager, Radiochemistry

Date

## **Appendix A**

### **Sample Irradiation Data**

## Appendix A

### Sample Irradiation Data

4 MRad Samples							
Initial temperature (°C) =				Final Temperature (°C)			
Sample Number	start	Stop	OD1	OD2	OD3	Filters	
						Blue	Yellow
							Green

10 MRad Samples							
Initial temperature (°C) =				Final Temperature (°C)			
Sample Number	start	Stop	OD1	OD2	OD3	Filters	
						Blue	Yellow
							Green

32 MRad Samples							
Initial temperature (°C) =				Final Temperature (°C)			
					Filters		
Sample Numberstart	Stop	OD1	OD2	OD3	Blue	Yellow	Green
Duration 1							
Duration 2							
Duration 3							
Σ							



## **Appendix B**

### **Known Hydrogen Samples**



## Appendix B

### Known Hydrogen Samples

Initial temperature (°C) =		Final temperature (°C) =	
Start Time:		Stop Time:	