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Hydrogen Retention and Release Summary from Tank 48H from September 1995 to October 1996 (U)

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SUMMARY

Investigations into the nature and extent of hydrogen releases from Tank 48H provide the following insights:

- Under current Tank 48H conditions and hydrogen generation rates, between 40 and 100% of the hydrogen produced is retained in Tank 48H during quiescent periods encountered. Further testing is required to clarify hydrogen retention at higher generation rates and inventories.

- Operation of pumps releases this hydrogen. As expected the release rate appears to increase as a function of the number of pumps operating.

- Hydrogen release stops when pumps stop.

- Measured radiolytic hydrogen generation rates agree with those previously observed during laboratory testing and reported in scientific literature.

- Hydrogen retention occurs with either floating or submerged tetraphenylborate solids.

These observations lead to the following recommendations.

- Additional Tank 48H and laboratory measurements should be made to quantify the ability of the slurry to retain hydrogen, to verify the radiolytic generation rates for hydrogen and to quantify the dependence of hydrogen release on pump operation. This report includes a preliminary matrix for such testing.

- Increased attention to the quality of the hydrogen measurements made by the gas chromatographs will improve the reliability of future measurements. For example, when hydrogen retention times deviate from specified tolerances corrective action (i.e., regenerating the column) should be taken.

INTRODUCTION

Since the addition of fresh material to Tank 48H in September of 1995, frequent measurements of the tank vapor space have been made. These measurements demonstrated hydrogen release from the slurry in the tank upon agitation. Previous laboratory work[1] proved that measurable quantities of hydrogen can be produced by radiolysis. Retention of hydrogen within Tank 48H may pose a potential safety concern.[2] High Level Waste Engineering requested the Waste Processing Technology Section to investigate the release of hydrogen from the tank.[3] This report outlines the results of that investigation with emphasis on the measured hydrogen generation rates and a summary of the hydrogen retention and release behavior.

DISCUSSION

Hydrogen Measurements

Since September of 1995, two gas chromatograph (GC) units have been used to sample the Tank 48H vapor space. These units can detect a number of gases in the vapor space including oxygen, nitrogen, benzene and hydrogen. Each of these species exhibits a specific retention time. Also, the characteristic retention time differs for each individual chromatographic column. Periodic calibration checks are performed on the equipment. Also, the columns are periodically regenerated by heating. The two units are designated GC1 and GC2. Calibration checks are performed with a gas known to contain approximately 0.1 vol % hydrogen. These calibration checks provide a good measure of the system performance. Figure 1 provides a plot of typical signals as a function of retention time for these calibration checks. Note that the typical hydrogen retention time for GC1 is between 14 and 15 seconds while the typical retention time for GC2 is between 12 and 13.5 seconds.

However, the GC units do not always associate the hydrogen signal with the appropriate retention times. Frequently samples report a retention time significantly shorter than indicated above. These signals are most likely associated with the fluctuation of the carrier gas flow and should be eliminated from the measurement data base when performing analyses. In addition, signals with retention times higher than expected are also reported. These signals may represent hydrogen, as the retention time for hydrogen increases as the chromatographic column is fouled by extensive use. However, calibration checks of the equipment following such degradation indicate that a severe loss of integrity in the measurements occurs as the retention time increases. In addition, extremely large retention times (more than twice typical retention times) have been found to provide false readings most likely associated with the measurement of other gases (i.e., oxygen and nitrogen).

Therefore, in developing the data employed in this study, any hydrogen signal with a retention time less than specified (14 seconds for GC1 and 12 seconds for GC2) from the calibration checks were eliminated. In addition, any data characterized by a retention time significantly later (more than 2 seconds) than the specified retention time were eliminated. Also, data characterized by increasing retention times may introduce some uncertainty in the results obtained herein. Note, however, that the majority of the data employed was characterized by retention times within the specified limits indicated above.

Another significant uncertainty exists in the measurements performed by these chromatographs. Typically, calibrations are performed at 100 ppm and 1000 ppm. However, the majority of these measurements were made at less than 100 ppm. Therefore this data contains a level of uncertainty associated with possible calibration error to consider when reviewing. Also, this source of error suggests the need for care in selecting calibration ranges to ensure the accuracy of future measurements.

Hydrogen Generation

Using the methodology outlined above, hydrogen measurements were collected from the extensive data base of ITP tank vapor space measurements (see Figures 2-8). These data were inspected for evidence of significant releases of hydrogen. Seven instances of measurable hydrogen release were identified. Each of these releases involved pump operation following a significant quiescent period. Table 1 outlines the timing and quantity of hydrogen released for each of these events.

The quantity of hydrogen released for each event was determined by integrating the quantity of hydrogen removed as a function of time by the nitrogen purge. The development of this integration is presented in Appendix 1. Note that all extensive quiescent periods in Tank 48H during the time period of interest were found to result in a hydrogen release upon mixing.

Table 1. Summary of hydrogen releases from Tank 48H.

Event #	Event Description	Event Time	Hydrogen Released (kg)	Percent LFL Obtained
1	2nd pump bump test	October 27, 1995	.024	0.040
2	3rd pump bump test	November 10, 1995	.065	0.045
3	VDS sample run	December 2, 1995	.040	0.175
4	Benzene Depletion	December 8, 1995	.053	0.063
5	Benzene Depletion	March 5, 1996	.19	0.113
6	Pre PVT-1	September 14, 1996	$.160 < x < .20$	0.065
7	PVT-1	October 23, 1996	$.21 < x < .58$	0.350

Note that during the quiescent periods prior to Events #6 and #7 (from August 30 to September 14 and from September 14 to October 23), significant vapor space hydrogen measurements were observed. Inclusion of these measurements results in the upper bound release masses (i.e., .20 and .58 kg, respectively) while the lower number represents only the hydrogen released during the specific event. The measurements obtained during these quiescent periods should be used cautiously since significant degradation in the hydrogen signal was observed during calibration checks over these dates.

From these measured hydrogen releases, one may determine the average rate of hydrogen production over the quiescent period preceding each pump operation. In developing this generation rate the time period employed was taken from the end of the previous pump operation to the end of the pump operation of interest. Also note that due to the short duration of the VDS sample run, the assumption cannot be made that the system was depleted of hydrogen at the conclusion of this operation. Therefore, Events #3 and #4 have been grouped together in determining a hydrogen generation rate. Similarly, Event #6 was also an abbreviated pump operation and was combined with Event #7. Radiolytic hydrogen generation rates are typically reported as G-values with units of molecules of hydrogen produced per 100 electron volts of radiation energy. Appendix 2 gives the development for the conversion of the observed hydrogen release to a measured G-value. Table 2 contains a list of the measured hydrogen G-values for the indicated events. Also presented in Table 2 is the duration of the quiescent period prior to each hydrogen release. For the cumulative release for Events #3 and #4, the quiescent period is taken as the period before Event #3. Again, the upper bound indicated for Events #6 and #7 should be used cautiously given the signal degradation over the measurement time period.

Table 2. Hydrogen G-values for hydrogen releases from Tank 48H.

Event	Duration of quiescent period (days)	Expected G-value[1] (molecules /100 eV)	Measured G-value (molecules /100 eV)
1	17	.097	.041
2	16	.097	.12
3-4	31	.097	.087
5	72	.097	.075
6-7	55	.156	$.20 < g < .41$

Previous laboratory measurements indicate that the anticipated hydrogen G-value under current Tank 48H conditions should fall between 0.097 and 0.156, depending upon solution nitrate and nitrite concentration.[1] Note that, given the uncertainties in the tank measurements, the values measured for Tank 48H agree well with these laboratory measurements. This result indicates that, under current tank conditions, the majority of the hydrogen generated in Tank 48H is retained during the quiescent periods and only released during periods of agitation. (This conclusion assumes that the quantity of hydrogen released increases approximately linearly as a function of the duration of the quiescent period.) Also note the measured generation values do not show a significant trend with the duration of the quiescent period. This result also indicates the majority of the hydrogen is retained within the slurry during quiescent periods. However, current Tank 48H conditions are characterized by relatively low hydrogen generation rates and, as such, the hydrogen inventories retained have been relatively small (as indicated in Table 2). The change in the expected G-value between Events #5 and #6 is due to the dilution of nitrate and nitrite in Tank 48H. The previous laboratory study provides an expression for the G-value as a function of the nitrate and nitrite concentrations. Repeated measurements of the nitrate and nitrite concentration indicated these concentrations were relatively constant prior to Event #5 and then decreased measurably prior to Event #6.

Two additional factors may influence the validity of this assertion. The solids concentration varied significantly over the time period of interest, being significantly lower for Events #1, #6 and #7. In addition, the solid tetraphenylborate phase floated during the first five events but sank for the final two release events. Thus, since the longer quiescent periods were experienced during the latter tests, the impact of extended quiescent periods is confounded with both the solids content in the tank and the location of the solids. Additional measurements that avoid such confounding are recommended.

Table 2 also contains expected G-values. These values are based on measured rates for salt solutions in the presence of KTPB solids and are primarily dependent on nitrate and nitrite ion concentrations. Note, however, that the final two events were characterized by a measurably higher hydrogen generation rate. The calculated values indicate that the rate of hydrogen production due to radiolysis is suppressed by the presence of nitrate ion in solution. During the period between the 5th and 6th hydrogen release event, a significant quantity of water was added to Tank 48H, producing at least a 35% reduction in the nitrate and nitrite concentration. As indicated in Table 2, this decrease would be anticipated to produce a 50% increase in the hydrogen G-value. Thus, the higher hydrogen generation rate for the 6th and 7th release events can be attributed at least partially to the decrease in the nitrate and nitrite concentration. Note that the solids content and location of the solids may also play a role in this observed trend.

Hydrogen Release

The measured hydrogen releases can also provide an indication of the ability to control the hydrogen releases from Tank 48H through pump operations. Figures 2 through 8 contains plots of the hydrogen measurements for each of the release events. Particular attention should be paid to release Events #2, #3, and #4. Inspection of Event #2 (Figure 3) indicates that, when the additional three pumps were turned on during this operation, the hydrogen release rate increased markedly. Also note that, while the hydrogen inventory at the start of Event #4 (Figure 5) was likely similar, if not greater than that of release Event #3 (Figure 4), the release rate is significantly lower during Event #4. The release rate for Event #3 was approximately 0.7 kg/hr while the release rate for Event #4 was approximately 0.006 kg/hr. This lower release rate can be associated with the use of only one pump at low speed during the Event #4 in contrast to 4 pumps at full speed in Event #3. Also note that while a significant hydrogen inventory existed during each of these events, the release of this hydrogen ceased very quickly after stopping pump operation. These limited findings indicate that hydrogen release can be controlled through the use of pump operation.

Note that the location of the GC sample was not identical for all of these events. During Events #5, #6 and #7, samples were drawn from the port location nearest to the slurry surface. During earlier release events, samples were drawn from all of the port locations. These earlier measurements indicates that the hydrogen profile was homogeneous throughout the tank. Therefore, while the measurements in the latter events were only from near the surface, they have been assumed to be representative of the bulk tank vapor space.

Proposed Path Forward

To provide additional insight into the nature of the hydrogen generation, retention and release within Tank 48H, it would prove useful to control the duration of future quiescent periods in Tank 48H prior to the anticipated addition of fresh waste. These quiescent periods should be of sufficient duration to afford the ability to measure significant hydrogen releases. A hydrogen inventory of 0.04 kg in Tank 48H would provide such a measure. In addition, it would prove useful to use longer quiescent periods to verify the assumption that hydrogen retention is constant over extended time periods. Furthermore, additional insight into the ability to control the hydrogen release through pump action can be obtained by using a variable number of pumps during these hydrogen measurement operations. From these calculations, preliminary calculations of mass transfer coefficients could be generated. Based on these considerations, operation of the pumps in Tank 48H along the guidelines in Table 3 would provide beneficial insight into the generation, retention and release of hydrogen in Tank 48H.

Table 3. Tank 48H pump operation guidelines.

Test #	# of pumps	Duration of quiescent period (weeks)
1	4	2
2	3	6
3	1	4
4	1	8
5	2	6
6	4	6
7	2	2
8	3	2

CONCLUSIONS

Since October of 1995, seven instances of significant hydrogen release from Tank 48H have been observed. All of these instances have been associated with operation of pumps within Tank 48H. These results indicate that hydrogen is stored in the slurry during quiescent periods and then released upon agitation of the tank. Furthermore, the quantities of hydrogen released are consistent with those expected based on previous laboratory measurements of radiolytic hydrogen generation rates. These results also suggest that additional measurements be performed in Tank 48H to verify the quantity of hydrogen that can be retained and the dependency of the release rate on pump operation. In addition, improvements in the quality of the hydrogen measurements should be made to ensure the validity of any future measurements of hydrogen retention and release.

REFERENCES

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[1] C.L. Crawford and D.D. Walker, "Hydrogen Generation by Radiolysis of Tetraphenylborate Solutions and Slurries (U)", WSRC-TR-96-0109, June 19, 1996.

[2] J.K. Thomas and T.E. Britt, "Potential Inadequacy: Gas Trapping in ITP Waste Tank (U)", EPD-DBA-94-0134, December 15, 1994.

[3] A.W. Wiggins, "Technical Task Request (U)", HLE-TTR-97020, November 20, 1996.

4 R. F. Swingle, "Calculation of Benzene Releases from Tank 48H (U)", WSRC-TR-96-0130, May 20, 1996.

5 R. C. Reid, J. M. Prausnitz and B. E. Poling, The Properties of Gases and Liquids, 4th Edition, New York, McGraw Hill, 1987.

Appendix 1

Calculation of Hydrogen Releases from Tank 48H

The calculation of hydrogen releases from Tank 48H is essentially the same as the calculation of benzene releases presented previously[4] and is based on the ideal gas equation. The only difference between the two calculations is the use of the hydrogen concentration from the gas chromatographs instead of the benzene concentration.

The GC hydrogen measurement is made on a stream of vapor taken from the Tank 48H vapor space. The vapor stream is dried (assumed completely dry) prior to being analyzed by the GC. The gas in the tank has a residence time of approximately 200 minutes and therefore is assumed to be completely humidified. The purge from the tank passes through a condenser to remove some of the moisture. The dew point of this stream is assumed to be the same as the effluent temperature from the condenser. The purge flow is then heated before passing through a blower to a flow meter. The following equation may be used to calculate the partial volume of hydrogen released from Tank 48H.

$$V = \frac{(C_{Hyd})(F_P)}{100}(t), \tag{1}$$

where V is the volume of hydrogen, C_{Hyd} is the GC hydrogen concentration in volume percentage, F_P is the purge flow rate in cubic feet per minute (cfm) and t is the time interval of the calculation in minutes. The purge flow data are provided in standard cubic feet per minute (scfm) which is cfm referenced to a "standard temperature" (25 °C) and pressure (1 atm). The hydrogen concentration must be corrected to account for the difference in humidity at the GC and at the point where the flow is measured. The following equation accounts for this difference.

$$C_{Hyd}^{purge} = C_{Hyd}^{GC}\left(\frac{760 - P_{H2O}^{purge}}{760 - P_{H2O}^{GC}}\right) \tag{2}$$

where C_{Hyd}^{GC} and C_{Hyd}^{purge} = the hydrogen concentrations in vol % at the GC and in the purge flow, respectively, and
P_{H2O}^{GC} and P_{H2O}^{purge} = the partial pressures of water in mm Hg at the GC and in the purge flow, respectively.

The system is assumed to be operating at 1 atmosphere or 760 mm Hg. Because the vapor stream at the GC is assumed to be completely dry, the P_{H2O}^{GC} term is eliminated. The vapor pressure of water at the condenser dew point may be calculated using the Wagner equation.

$$\ln P_{vpr} = \frac{a\tau + b\tau^{1.5} + c\tau^{3} + d\tau^{6}}{T_r} \tag{3}$$

where P_{vpr} = the reduced vapor pressure ((vapor pressure)/(critical pressure) in bar; critical pressure is 221.2 bar for water),
T_r = the reduced temperature ((temperature)/(critical temperature) in K; critical temperature is 647.3 K for water),

τ = $(1-T_r)$ and
a, b, c and d = are constants (-7.76451, 1.45838, -2.7758 and -1.23303, respectively, for water).[5]

The temperature used for the humidity calculation is the ventilation condenser effluent temperature converted to K. The vapor pressure of water in the purge stream may be calculated using the following equation.

$$P_{H2O}^{purge} = e^{\ln(P_{vr})} P_{H2O}^{C}(750), \tag{4}$$

where P_{H2O}^{C} is the critical pressure of water (221.2 bar) and 750 is the conversion from bar to mm Hg.

If this calculation is completed using an EXCEL® spreadsheet, the time/date functions may be used. EXCEL® assigns a number to each day and time, with one day being equal to 1.00. For each set of data, there is an associated date and time. The time interval, in minutes, of each calculation was calculated by the following.

$$t = (D_2 - D_1)(24)(60) \tag{5}$$

where D_1 and D_2 are the date/time for the start and ending of the calculational time interval.

R is the ideal gas constant and may be expressed in a number of different quantities. For this calculation, units of (L*atm)/(g-mole*K) are used, with a value of 0.08205. The temperature used for this calculation is the reference temperature for the flow rate. This temperature is 25 °C or 298.15 K. A conversion factor (28.316 L/ft^3) is also used to convert the purge flow rate to L/m.

Combining equations gives the number of g-moles of hydrogen released during the calculation interval.

$$n = \left(\frac{\left(\left(\frac{\left(C_{Hyd1}^{purge} + C_{Hyd2}^{purge}\right)}{2}\right)/100\right)\left(\frac{F_{P1} + F_{P2}}{2}\right)(28.316)(t)}{(0.08205)(298.15)} \right) \tag{6}$$

This can be converted to grams by multiplying by the molecular weight of hydrogen in g/g-mole (2.016). The releases over individual calculational intervals may be summed to give the releases over larger intervals.

For the purposes of this calculation, the value of the hydrogen concentration has been taken from the results from Tank 48H GC#1. An average of both GCs may be used instead.

Appendix 2

Calculation of Hydrogen G-value for Tank 48H

The g-value for the generation of hydrogen from energy produced by the radioactive decay of ^{137}Cs can be calculated from the following equation.

$$g = \frac{n_{Hyd}}{\dfrac{(kCi_{Cs})(E_{Cs})}{1.602E-19}} \Bigg/ (t)(100), \qquad (1)$$

where g is the number of molecules of hydrogen produced per 100 eV of energy produced from the decay of ^{137}Cs,
n_{Hyd} is the total number of molecules of hydrogen produced during a given time period,
kCi_{Cs} is the number of kilocuries of ^{137}Cs in Tank 48H (currently ~400),
E_{cs} is the energy released by the decay of 1 kCi of ^{137}Cs (4.84 W),
1.602E-19 is the conversion from watts to eV/s,
t is the time interval of concern (s) and
100 is used because g is given in units of # molecules/100 eV.

Figure 1. Signal vs Retention Time

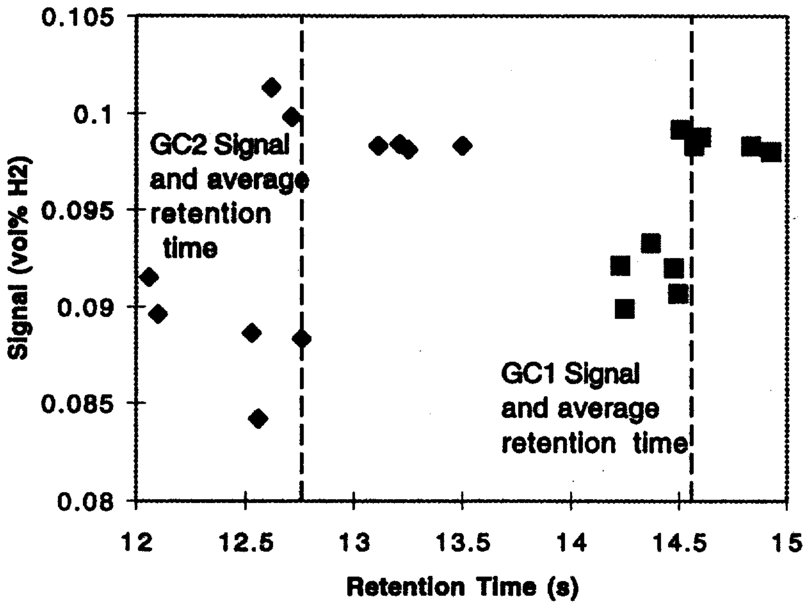


Figure 2. Vapor Space Hydrogen concentrations for 2nd Pump bump Test

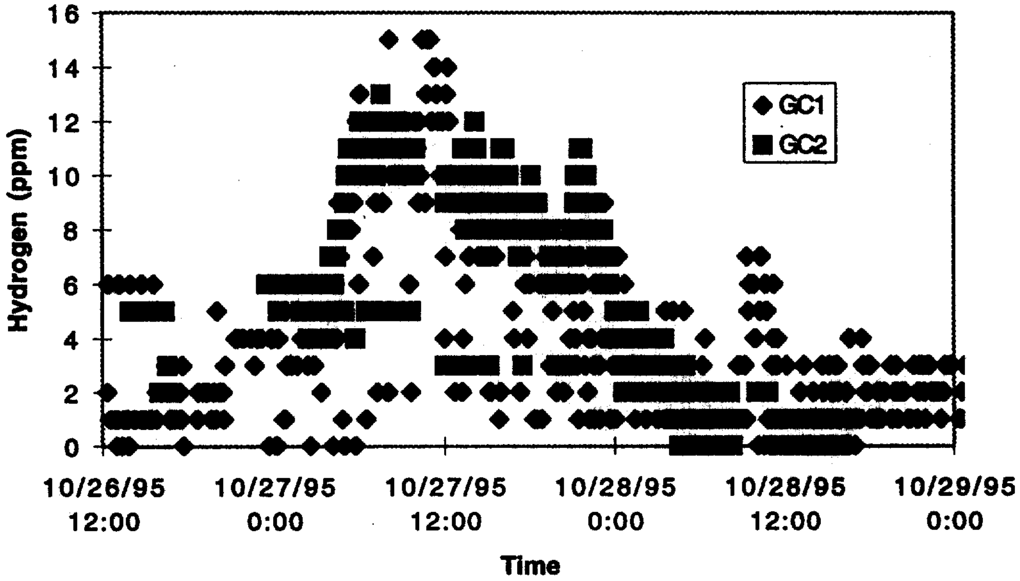


Figure 3. Vapor Space Hydrogen Concentrations for 3rd Pump Bump Test

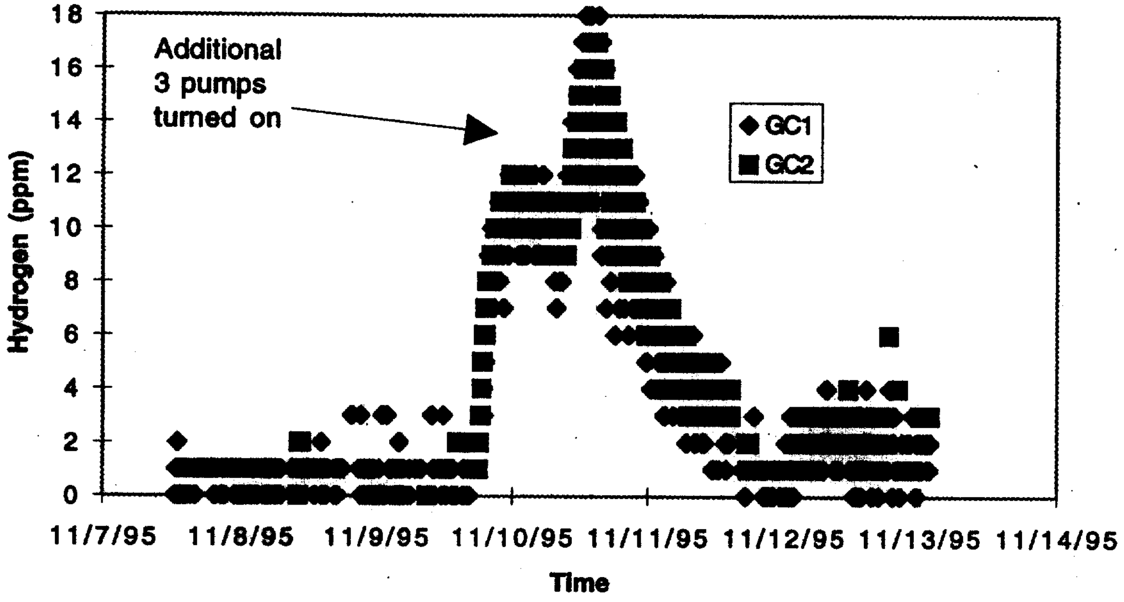


Figure 4. Vapor Space Hydrogen Concentrations for VDS sample run

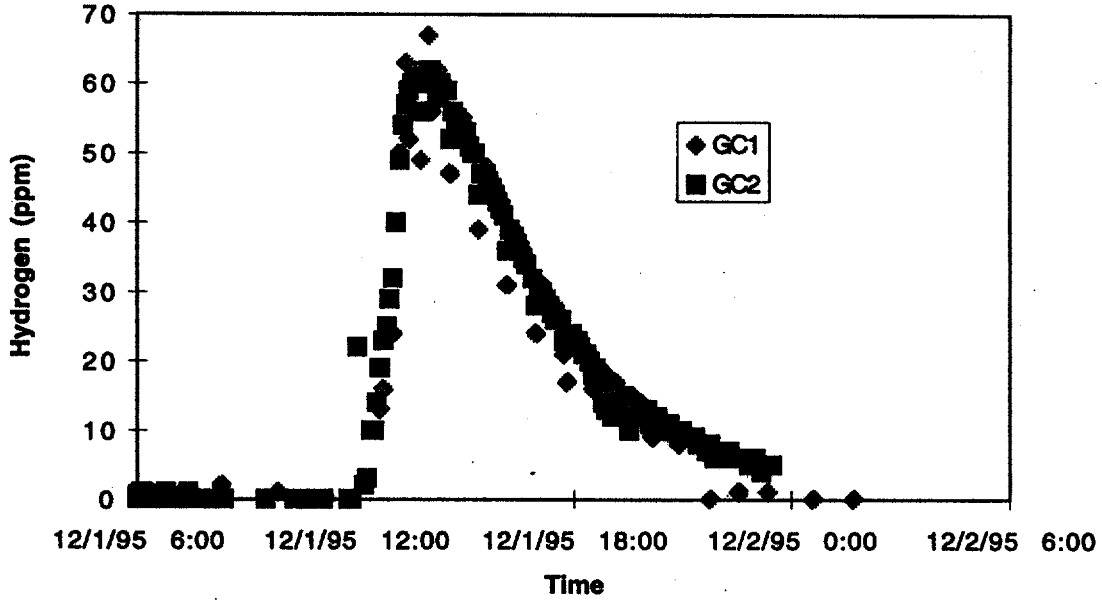


Figure 5. Vapor Space Hydrogen Concentrations for Benzene Depletion Runs

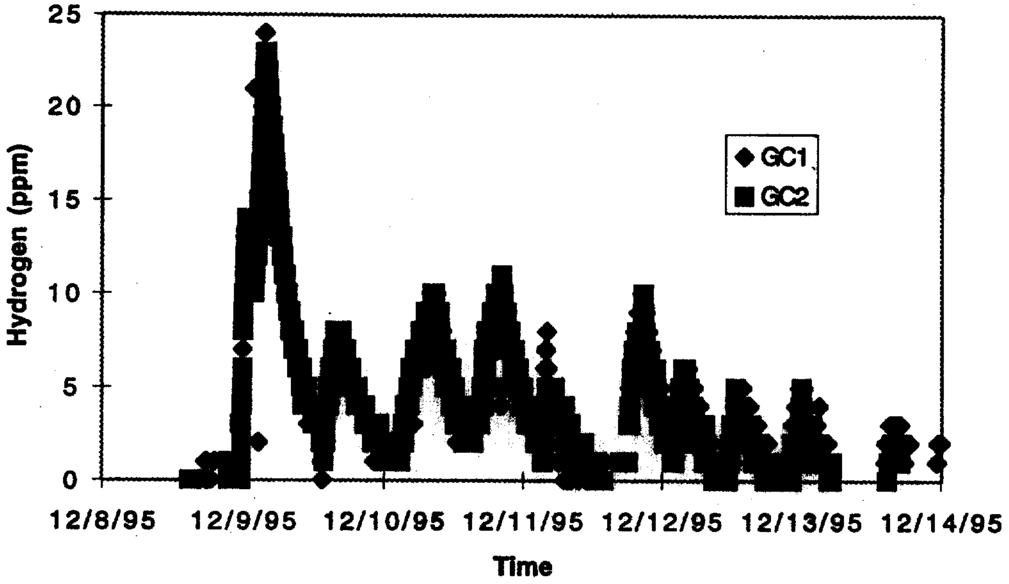


Figure 6. Vapor Space Hydrogen Concentrations for Benzene Depletion Runs

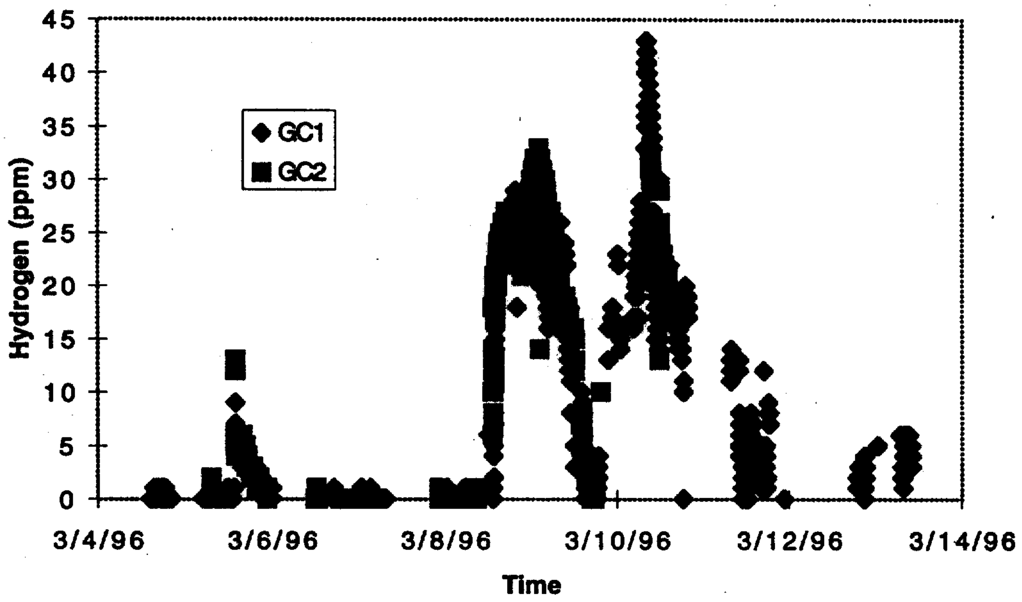


Figure 7. Vapor Space Hydrogen Concentrations for Pre PVT-1

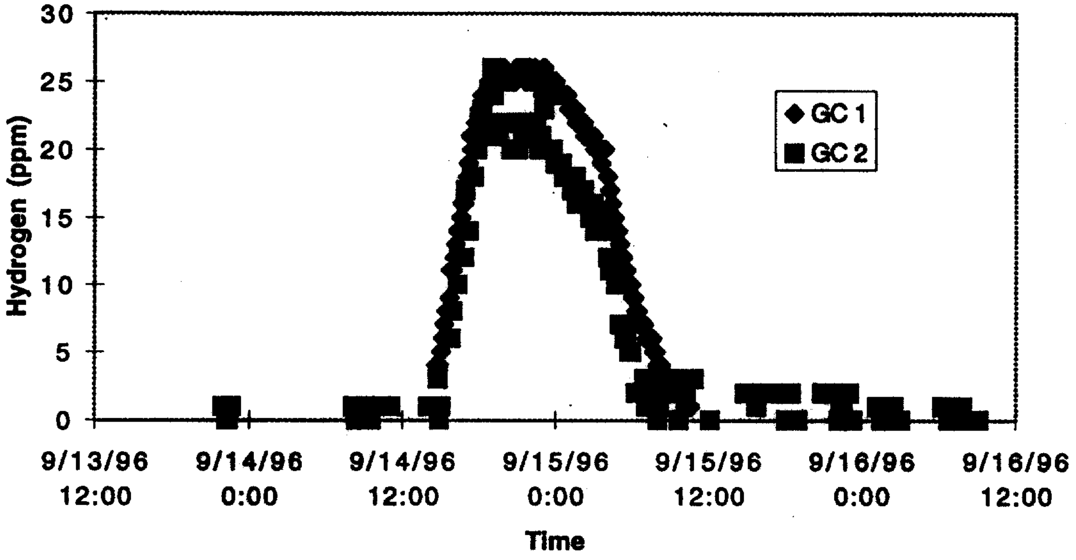
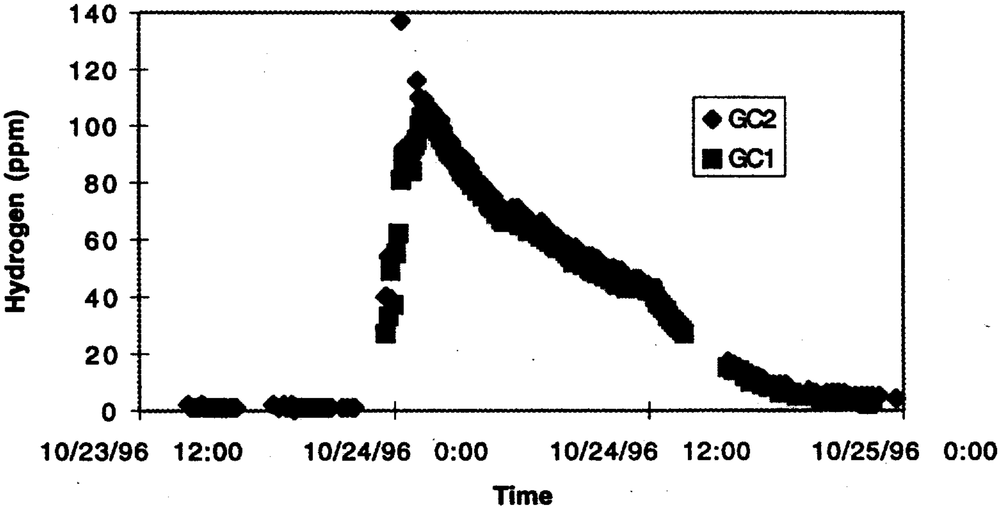


Figure 8. Vapor Space Hydrogen Concentrations for PVT-1



D.B.Amerine, 241-121H
M.J.Barnes, 773-A
N.E.Bibler, 773-A
T.E.Britt, 732-B
J.T.Carter, 704-25S
G.L.Cauthen, 241-119H
M.C.Chandler, 703-H
W.C.Clark, 704-56H
C.L.Crawford, 773-41A
P.D.d'Entremont, 703-H
D.E.Doughty, 704-56H
S. Eberlein,704-56H
H.H.Elder, 704-S
T.J.Fiske, 241-120H
J.R.Fowler, 241-121H
M.S.Hay, 773-A
J.R. Hester, 703-H
M.J.Hitchler, 992W-1
D.T.Hobbs, 773-A
M.L.Hyder, 773-A
R.A.Jacobs, 704-T
M.D.Johnson, 704-56H
M.T.Keefer, 704-56H
T.J.Lex, 719-4A
B.L.Lewis, 703-H
J.C.Marek, 704-T
J.E.Marra, 704-56H
J.D.Menna, 730-2B
M.S.Miller, 704-56H
M.J.Montini, 704-S
J.P.Morin, 719-4A
C.A.Nash, 676-1T
J.K.Norkus, 730-2B
L.M.Papouchado, 773-A
R.A.Peterson, 676-T
P.L.Rutland, 241-152H
R.M.Satterfield, 719-4A
P.C.Suggs, 703-H
R.F.Swingle, 773-A
W.L.Tamosaitis, 773-A
G.A.Taylor, 703-H
T.C.Temple, 703-H
J.K.Thomas, 730-2B
W.B.VanPelt, 676-1T
D.D.Walker, 773-A
W.R.Wilmarth, 773-42A
A.W.Wiggins, 241-152H
G.T.Wright, 773-A
TIM, 703-43A
LWP Files c/o A. Patterson 773-A
ITP Files c/o L. Sumner, 704-56H