97-0002509

Department of Energy
Savannah River Operations Office
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JUL 30 1997

The Honorable John T. Conway
Chairman, Defense Nuclear Facilities Safety Board
625 Indiana Avenue, N.W., Suite 700
Washington, D.C. 20004

Dear Mr. Chairman:

SUBJECT: Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 96-1 Deliverable - Report on Bounding Mass Transfer Coefficients

Enclosed is the subject report which provides a scheduled deliverable (Commitment 5, Milestone 5.2.4-2) in accordance with the DNFSB Recommendation 96-1 Implementation Plan. This report, "Bounding Mass Transfer Coefficients for the In-Tank Precipitation Facility (U)" (HLW-OVP-97-0052, Rev 1), discusses the application of the mass transfer coefficients for benzene in each of the In-Tank Precipitation (ITP) tanks. Also enclosed are three supporting reports: "Confidence Limits for Mass Transfer Coefficients for Benzene Release From Tank 48H and 49H (U)" (WSRC-TR-97-0167) and "Updated Estimates of Mass Transfer Coefficients in Tank 50H, Salt Solution Hold Tank, Flush Water Receipt Tank and Low Point Drain Tank (U)" (WSRC-TR-97-0056, Rev 1) which develop bounding mass transfer coefficient estimates for the ITP tanks; and "Estimates of Mass Transfer Coefficients in Tank 50H and 48H (U)" (WSRC-TR-97-229) which describes the methods used to estimate actual mass transfer coefficients based on plant measurement data.

The model-based estimates of bounding mass transfer coefficients are only applicable in the absence of readily releasable benzene. Therefore, pending the outcome of work being performed to satisfy Milestone 5.2.4-4 (Establish bounding benzene release rates that could occur during all planned and inadvertent ITP plant evolutions), a more conservative mass transfer rate associated with readily releasable benzene would have to be applied. This work is expected to provide additional data which may allow use of the model-predicted bounding mass transfer rates rather than the more conservative rates associated with readily releasable benzene. Copies of the subject deliverable have been provided and discussed with your staff.

Please direct any questions to me or W. F. Spader at (803) 208-7409.

Sincerely,

Frank R. McCoy, ~~III~~
Assistant Manager for
High Level Waste

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HLW-OVP-97-0052, Rev. 1

Bounding Mass Transfer Coefficients
for the
In Tank Precipitation Facility (U)

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7/23/97

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Bounding Mass Transfer Coefficients
for the
In-Tank Precipitation Facility (U)

1.0 INTRODUCTION

The In-Tank Precipitation (ITP) facility at the Savannah River Site initiated radioactive operation in Tank 48H in September 1995. During pump operation in December 1995, benzene evolved from Tank 48H at higher rates than expected, though the limiting condition of operation was never approached. Subsequent investigations revealed the source of benzene was catalytic decomposition of excess, soluble tetraphenylborate ion (TPB-) that was added to assure adequate suppression of cesium solubility [reference 1].

In August, 1996 the Defense Nuclear Facilities Safety Board (DNFSB) issued Recommendation 96-1 in which the Board recommended that the Department of Energy develop a better understanding of the mechanisms of benzene generation, retention, and release. In the 96-1 Implementation Plan [reference 2], the Department of Energy developed its approach to resolve the issues raised by the DNFSB. The plan is based on the development of a revised safety strategy and a combination of bench, pilot scale and plant tests aimed at understanding benzene generation, retention, and release. Further, the test program includes these elements:

- Benzene generation
  + determine catalyst(s), mechanisms, and rate constants for decomposition of soluble TPB-
  + study stability of solid CsTPB and KTPB
  + confirm using actual wastes
- Benzene retention
  + determine capacity of slurries to retain benzene
  + endeavor to understand the physical forms in which benzene is retained
- Benzene release
  + develop an understanding of how benzene is released in lab scale tests and in pilot scale demonstration
  + determine mass transfer coefficients associated with plant equipment operational configurations

The Implementation Plan provides a commitment to quantify benzene release rates for both planned and inadvertent plant evolutions. As part of this commitment, Milestone 5.2.4-2 is to Define Bounding Mass Transfer Coefficients for ITP Tanks. This report, combined with references 3, 4, and 5 meets this milestone. This report describes how the mass transfer coefficients for benzene may be used in the operation of each tank in the ITP Facility. References 3 and 4 describe the calculation of the bounding mass transfer coefficients for tank operating conditions. Reference 5 describes the methodology used to extract mass transfer coefficients from tank vapor space benzene measurement data. Descriptions of tank operating strategy may be found in reference 6.

2.0 APPLICATION OF MASS TRANSFER COEFFICIENTS

Safe operation of the ITP process requires an understanding of mass transfer coefficients for slurries containing benzene, to address two types of scenarios. First, the upper bound on mass transfer under specific conditions is required to ensure that the amount of benzene released into the vapor space in a given time period does not cause the vapor space concentration to exceed a defined limit. (The limit is different for different scenarios, and will be defined in the final report for Milestone 5.2.1-3 of the Recommendation 96-1 Implementation Plan [reference 2].) Second, the lower bound on mass transfer under specific conditions would be necessary to understand the amount of time required to deplete the slurry of retained benzene, unless benzene depletion can be confirmed through measurement of benzene in the vapor space. The use of a lower bounding mass transfer coefficient depends upon effective pump mixing to deplete benzene at all proposed ITP operating conditions. Discussion of the approach actually applied for defining pump operation duration in ITP will be included in the report for Milestone 5.2.1-3 of the Recommendation 96-1 Implementation Plan [reference 2].

The proposed operational strategy [reference 6] for ITP tanks includes periodic operation of slurry pumps to deplete the slurry of benzene. The period of time between pump runs (i.e. pump operation frequency) must be defined so that release of the accumulated benzene does not exceed a predetermined limit. The amount accumulated is the benzene generation rate multiplied by the length of time since the pumps were last run to deplete benzene. The amount of benzene released in a subsequent pump run is a function of both the accumulated quantity and the mass transfer coefficient. The upper bounding mass transfer coefficients associated with pump operation need to be applied to calculate pump run frequency.

3.0 MASS TRANSFER COEFFICIENTS FOR TANKS 48 AND 49

Frequency of Slurry Pump Operation

Reference 3 describes the development of upper bounding mass transfer coefficients for Tanks 48 and 49 during the operation of four slurry pumps. In Tank 48, data was only available at three weight percent slurry and a volume of approximately 160,000 gallons. No data was available from Tank 49 to confirm the modeled values described in reference 3. However, the data from Tank 48 may be applied by considering two key differences between the tanks:

1. The material in Tank 49 will contain a higher proportion of solids, which will tend to increase the viscosity of the waste and therefore lower the mass transfer coefficient.

2. The slurry pumps in Tank 49 are more powerful than the pumps in Tank 48. Operation of the pumps at high speed would tend to increase the mass transfer coefficient. To overcome this possible non-conservatism, pump operation will initially be restricted to lower speed while collecting additional data.

Operation of the pumps in Tank 49 can be configured so that the mass transfer coefficients measured in Tank 48 are conservative with respect to Tank 49. The more conservative of the values calculated for Tank 48 or 49 may then be applied to Tank 49. When actual measurement data is acquired from Tank 49 after resumption of waste processing, it may be possible to relax the conservatism.

Tables 1 and 2 below are reproduced from reference 3, and define the model-predicted bounding mass transfer coefficients under a number of operating conditions for Tanks 48 and 49.

Table 1. Estimated and confidence limit mass transfer coefficients for Tank 48H with 4 pumps operating.

			Mass Transfer Coefficients	
	Weight Percent Solid	Tank Level (kGal)	Estimated at Ambient Conditions (10^{-5}m/s)	95 % Confidence Limit at Limiting Conditions (10^{-5}m/s)
Start of typical 1st batch	1.0	600	1.3	7.8
End of typical 1st batch	4.0	150	1.0	5.0
Start of typical 2nd batch	1.8	600	1.3	7.8
End of typical 2nd batch	7.0	150	0.6	2.9
Start of typical 3rd batch	2.5	600	1.3	7.8
End of typical 3rd batch	10.0	150	0.5	2.3

Table 2. Estimated and confidence limit mass transfer coefficients for Tank 49H with 4 pumps operating.

			Mass Transfer Coefficients	
	Dose Received (Mrad)	Tank Level (kGal)	Estimated at Ambient Conditions (10^{-5}m/s)	95% Confidence Limit at Limiting Conditions (10^{-5}m/s)
Start of Cycle 2	0	200	1.0	3.0
End of Cycle 2	70	110	2.8	8.4
Start of Cycle 3	30	270	1.9	5.7
End of Cycle 3	100	150	2.6	7.8
Start of Cycle 4	60	300	2.2	6.5

The mass transfer coefficients developed in reference 3 are anticipated to bound Tank 48 and Tank 49 operating conditions. However, under conditions of very high benzene accumulation, benzene has been observed to be retained in a form which is "readily releasable". Under these conditions, the mass transfer coefficient developed in reference 3 is not applicable. The mass transfer rate associated with free benzene would be bounding. Studies are underway [reference 7] to identify the change in benzene retention mechanism that gives rise to readily releasable benzene, and to determine conditions under which this retention mechanism can occur. These studies include examining the effects of floating solids on benzene release. The results of these studies will be reported in Milestones 5.2.3-1 and 5.2.4-4 of the Implementation Plan for Recommendation 96-1 [reference 2], describing benzene retention and release mechanisms. It is the intention of the facility never to operate under conditions of very high benzene accumulation. It is possible that studies will not quantify exactly what changes in conditions give rise to readily releasable benzene (e.g. a specific benzene concentration). If it cannot be shown that operating conditions will preclude formation of readily releasable benzene, the more conservative mass transfer rate associated with free benzene may need to be applied to determine allowable operating conditions.

Conclusion: The mass transfer rate associated with free benzene clearly bounds the mass transfer rates expected in tank operations. Additional information to be provided before finalizing the report for Milestone 5.2.1-3 of the Recommendation 96-1 Implementation Plan [reference 2] may allow relaxation of the rates to those described in Tables 1 and 2.

Duration of Slurry Pump Operation to Deplete Benzene

Lower bounding estimates of benzene mass transfer for Tanks 48 and 49 have not been developed. The length of time required for the pump operation to deplete the slurry of benzene in Tanks 48 and 49 will be determined based on vapor space benzene measurements rather than calculated. After benzene concentration in the vapor space has peaked and returned to a predetermined low level, the slurry will be considered to be sufficiently depleted of benzene to cease pump operation. The specific benzene value in the vapor space, and the corresponding benzene concentration in the slurry, will be defined based on measurement data and vapor-liquid equilibrium testing [reference 8]. The results of this work will be reported in Milestone 5.2.4-4 of the Recommendation 96-1 Implementation Plan [reference 2].

An understanding of the effectiveness of slurry pumps for forcing release of retained benzene is being developed to support finalization of the Authorization Basis, and will be described in Milestone
5.2.1-3 of the Recommendation 96-1 Implementation Plan [reference 2].

Conclusion: The lower bounding mass transfer coefficient during pump operation is not required because measurement data in the vapor space will be used to determine pump operation duration.

4.0 MASS TRANSFER COEFFICIENTS FOR TANK 50

Tank 50 will contain either filtrate or wash water. Organic precipitate solid material (which increases the ability to retain benzene) will not be transferred into Tank 50, thus reducing the concern regarding readily releasable benzene. Trace amounts of organic precipitate may be present due to precipitation of soluble TPB- with potassium present in Tank 50.

Frequency of Pump Operation

Bounding mass transfer coefficients have been developed for several pump operation scenarios [reference 4]. Table 2 of reference 4 (reproduced as Table 3 below) shows the bounding mass transfer coefficients for operation of two pumps in Tank 50, with either filtrate or wash water. These numbers may be used to bound the releases from Tank 50 if it can be shown that readily releasable benzene does not pertain to Tank 50. (The results of studies regarding benzene retention and release will be reported in Milestones 5.2.3-1 and 5.2.4-4 of the Recommendation 96-1 Implementation Plan [reference 2]). Until the potential for readily releasable benzene in Tank 50 is understood, the mass transfer rate associated with free benzene provides the bounding value.

Table 3. Bounding Mass Transfer Coefficients for Tank 50H

	Estimated Bounding Mass Transfer Coefficients (m/s) (a)	
# Pumps	**with Filtrate (~5 M Na^+)**	**with Wash Water (~2M Na^+)**
1 Pump Operation	3.9E-05 - 6.3E-05	7.6E-05 - 1.2E-04
2 Pump Operation	4.6E-05 - 7.5E-05	9.8E-05 - 1.5E-04

(a) The range of mass transfer coefficients given reflects the range of available liquid volumes (140 to 1,000 kGal); it does not indicate the accuracy or precision of the calculations.

Duration of Pump Operation to Deplete Benzene

The length of time required for the pump operation to deplete waste of benzene will be determined based on vapor space benzene measurements, as described for Tanks 48 and 49. Because of the low benzene generation and retention rates anticipated in Tank 50, vapor space measurement of benzene below the detection limit is anticipated. If benzene cannot be detected, an alternative approach to determining pump run duration in Tank 50 is to apply the lower bounding mass transfer coefficient to the duration of the pump operation. Reference 5 includes best estimate mass transfer coefficients for the quiescent case (2.6E-07), as well as one and two pumps operating (9.7E-07 and 1.5E-06 respectively, based on a tank volume of 720 kGal). In this case, the more conservative of the quiescent value or the lower 95% confidence interval bound for single pump operation (at the appropriate tank volume) would be used as a lower bounding mass transfer coefficient. Application of this number would require that the waste material be adequately mixed. Since Tank 50 contains minimal organic precipitate solids, achieving and showing adequate mixing is expected to be less problematic than in Tanks 48 and 49. However, the potential to accumulate precipitate solids or foam in Tank 50, thereby lowering the rate of mass transfer, must be evaluated. If a lower bounding mass transfer rate calculation is to be applied to Tank 50, discussion of mixing effectiveness and the impact on the mass transfer rate will be included in Milestone 5.2.3-1 of the Recommendation 96-1 Implementation Plan [reference 2].

5.0 PATH FORWARD

Based on current understanding, only the upper bounding mass transfer coefficients during pump operation are of importance to ITP. Actual measurement of benzene in the vapor space during pump operations will be applied rather than calculating lower bounding mass transfer coefficients. If benzene cannot be measured in the tank, a conservative lower bound will be applied while obtaining additional data.

Conservatism of Upper Bounding Coefficients

Since the mass transfer coefficients are confounded by the uncertainty regarding readily releasable benzene, the more conservative mass transfer rate associated with the evaporation of free benzene is currently considered the bounding mass transfer coefficient. Evaluation of the conditions leading to readily releasable benzene is underway, and may lead to relaxation of this constraint. The following questions must be addressed:

- What conditions must exist to support the formation of readily releasable benzene?
- Can specific threshold values be assigned to the conditions to ensure that readily releasable benzene does not form ? (E.g. if readily releasable benzene depends on benzene concentration, can a conservative concentration threshold be defined, below which no readily releasable benzene occurs?)
- Can controls be put in place to ensure that the conditions preventing readily releasable benzene are maintained?
- Can measurements be performed which confirm the absence of readily releasable benzene?

If the issue of readily releasable benzene is resolved, then the model-developed mass transfer coefficients may be applied in the range of conditions under which they have been shown to be conservative. Additional data collection is required to confirm the model over the full range of conditions.

Further Data Collection

Further data to refine mass transfer coefficients and relax conservatisms should preferably be acquired from tests in the tank under conditions that produce measurable quantities of benzene. Since the model has not been validated with measurement data over the full range of operating conditions, operations using the model-generated numbers may be restricted to conditions near those for which data is available. Alternatively, the more conservative numbers associated with evaporation of free benzene may be applied during initial operations.

Application of In-Tank Measurement Data

Reference 5 describes in detail two approaches that were used to regress tank vapor space and liquid benzene measurement data to produce estimates of mass transfer coefficients. The best fit output of these approaches depends on a number of assumed and measured input values. The form of the Henry's Law equation used to establish the vapor liquid equilibrium is of particular importance. Information that will clarify the vapor liquid equilibrium relationship is being developed as part of the Recommendation 96-1 resolution program (reference 8). The work in reference 5 used the best information currently available. The vapor liquid equilibrium information used in reference 5 is more current than that used in the previous calculations shown in references 3 and 4. In addition, a review of the Tank 48 data used in reference 3 allowed better definition of the tank volume for calculations in reference 5. The global minimum search routine applied in reference 5 was more sophisticated than that in reference 4. An error in the activiation energy used in the calculations in reference 4 was also corrected in reference 5. Hence the best estimate mass transfer coefficients from tank data shown in reference 5 are likely more accurate than those in references 3 and 4. As more information is gained, the inputs to the calculation method will continue to improve. This revision to the inputs in the calculation has no effect whatsoever on the calculated bounding mass transfer coefficients. The revised estimates from tank data continue to confirm that the calculated bounding values are, in fact, bounding.

6.0 REFERENCES

1. D. D. Walker, M. J. Barnes, C. L. Crawford, R. F. Swingle, R. A. Peterson, M. S. Hay, and S. D. Fink., *Decomposition of Tetraphenylborate in Tank 48H (U)*, WSRC-TR-96-0113, May 1996.

2. Department of Energy Implementation Plan for **Defense Nuclear Facility Safety Board Recommendation 96-1 to the Secretary of Energy**, Revision 0, October 1996.

3. R. A. Peterson, *Confidence Limits for Mass Transfer Coefficients for Benzene Release from Tank 48H and 49H (U)*, WSRC-TR-97-0167, Rev. 1, June 1997.

4. R. F. Swingle, R. A. Peterson and M. R. Poirier, *Updated Estimates of Mass Transfer Coefficients in Tank 50H, Salt Solution Hold Tank, Flush Water Receipt Tank and Low Point Drain Tank (U)*, WSRC-TR-97-0056, Rev. 1, July 1997.

5. R. A. Peterson and R. F. Swingle, *Estimates of Mass Transfer Coefficients in Tank 50H and 48 H (U)*, WSRC-TR-97-0229, July, 1997.

6. M. J. Montini, *ITP Safety Strategy for Tanks 48, 49 and 50 Deflagrations (U)*, WSRC-TR-97-0003, January 1997.

7. HLE-TTR-97018, *Benzene Retention and Release Beyond the Apparent Solubility Limit (U)*, November 14, 1996.

8. HLE-TTR-97017, *Apparent Benzene Solubility and VLE in KTPB Slurry (U)*, November 14, 1996.

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Keywords: Mass Transfer Coefficients
In-Tank Precipitation
Saltstone
Benzene

Retention Time: Permanent

Updated Estimates of Mass Transfer Coefficients in Tank 50H, Salt Solution Hold Tank, Flush Water Receipt Tank and Low Point Drain Tank (U)

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M. R. Poirier

Publication Date: June 16, 1997

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SUMMARY

This report provides best estimate and bounding estimate mass transfer coefficients for Tank 50H and the Salt Solution Hold Tank (SSHT), the Flush Water Receipt Tank (FWRT) and the Low Point Drain Tank (LPDT). The best estimate mass transfer coefficients derive from tank data using a previously documented mass transfer model. These mass transfer coefficients update those previously issued and include a better understanding of the benzene generation rates. The best estimate mass transfer coefficients for the SSHT, FWRT and LPDT use an empirical method proposed by Kawase and Moo-Young (K/M-Y). The bounding estimate mass transfer coefficients also derive from the K/M-Y method with an added uncertainty allowance based on the experimental uncertainty presented by K/M-Y with an additional allowance for temperature effects in the tanks. These calculations gave the following mass transfer coefficients

	Mass Transfer Coefficient (m/s) (d)		
	Tank 50H Filtrate	Tank 50H Wash Water	SSHT (c)
Best Estimate	3.0E-06 (a)	2.1E-05 (a)	1.6E-05
Bounding Estimate	7.5E-05 (b)	1.5E-04 (b)	7.6E-05

(a) Tank Volume = 720,000 gal, two pumps operating

(b) Tank Volume = 140,000 gal, two pumps operating

(c) Tank Volume = 8,900 gal, agitator running.

(d) All mass transfer coefficients calculated using the Kawase/Moo-Young method described below except the best estimate for filtrate in Tank 50H which derived from Tank 50H data.

Because of the paucity of the Tank 50H data, the mass transfer coefficient estimates for Tank 50H include considerable uncertainty. The mass transfer coefficients for the other tanks also include uncertainty, since the model used to predict them remains unproven with the Saltstone system.

INTRODUCTION

Because benzene may form downstream of the ITP process from the decomposition of phenylborates, concerns arise about the possibility of exceeding lower flammability limits in vessels such as Tank 50H, the SSHT, the FWRT and the LPDT. Because of these concerns, researchers examined the generation of benzene and the transfer of benzene from the liquid to the vapor phases in those tanks. This study responds to a request that the Waste Processing Technology Section (WPTS) review mass transfer coefficients previously documented in Reference 1.[2] Researchers examined mass transfer coefficients for Tank 50H. Researchers also estimated mass transfer coefficients in the SSHT, FWRT and LPDT using the Tank 50H values as a basis.

DISCUSSION

Tank 50H Mass Transfer Coefficients from Data

From September 1995 through January 1996, personnel made a number of measurements of benzene concentration in Tank 50H. These included measurements of both liquid and vapor phase benzene concentration. Previously, researchers used these measurements to develop estimates of mass transfer coefficients for Tank 50H.[1] (Note: A future report will more completely describe the method to regress mass transfer coefficients from tank measurements.) The basic equations in the model used to calculate the mass transfer coefficients follow.

$$\frac{dy}{dt} = \frac{kA(m(x) - y) - yQ(t)}{V_y} \text{ and } \tag{1}$$

$$\frac{dx}{dt} = \frac{G(t) - kA(m(x) - y)}{V_x}, \tag{2}$$

where k = the mass transfer coefficient calculated by this model,
x and y = the measured benzene concentration in the liquid and vapor benzene concentration from measurements,[1]
$G(t)$ = the benzene generation rate calculated by this model,
$m(x)$ = the vapor-liquid equilibrium expression (i.e., Henry's Law), measured experimentally,[3]
$Q(t)$ = the tank ventilation rate,
A = the surface area available for mass transfer (i.e., the tank liquid surface area),
V_x and V_y = the volume of liquid and vapor spaces, and
t = time.

Reference 1 provides the derivation and solution of these equations.

The mass transfer coefficient estimates originally obtained from this model assumed benzene generated from soluble sodium tetraphenylborate (NaTPB) with first order kinetics at a reference generation rate of 32.4 µg/L•hr for 30 °C and an activation energy of 140 kJ/mole.[1] The calculation did not account for the decrease in benzene generation rate as the NaTPB concentration decreased. However, analysis of the Tank 50H contents suggest that sufficient K^+ existed during the period of interest to cause precipitation of essentially all soluble TPB^-. Experience indicates that the decomposition of KTPB solids will occur slowly under Tank 50H conditions. However, significant quantities of 3PB likely transferred to Tank 50H with filtrate from Tank 48H. The decomposition of 3PB to benzene occurs in the presence of copper. This decomposition occurs via a first order reaction. The current calculation conservatively assumes each mole of 3PB decomposes to three moles of benzene with a first order rate constant and an activation energy of 71 kJ/mole.[4] (The activation energy derives solely from a study of copper-catalyzed decomposition of 3PB. The rate constant used, 0.0012 hr^{-1}, and the initial 3PB concentration, 81 mg/L, derives from regression of the Tank 50H data. The benzene generation rate is assumed to decrease with decreasing 3PB concentration in Tank 50H.) The obtained mass transfer coefficients agree within a factor of three with the previously calculated mass transfer coefficients. Table 1 gives the calculated mass transfer coefficients for a referenced tank volume of 720,000 gal (approximate Tank 50H volume during early December 1995). The mass transfer coefficient in Tank 50H data regression model varies directly with number of operating pumps and to the -1/3 power with tank liquid volume. Actual tank liquid volumes were used in the model. The current analysis fits the data better than the previous analysis. (The correlation coefficient approaches 0.94 for the current analysis and 0.87 for the previous analysis.) Figures 1 and 2 give plots of predicted and actual vapor phase benzene concentration data for December 1995 through January 1996. Figure 3 plots the predicted and actual liquid phase benzene concentration data for the same period. Figure 4 provides a plot of the variation in best estimate mass transfer coefficients with volume for Tank 50H.

Table 1. Calculated Benzene Mass Transfer Coefficients for Tank 50H

Operational Status	Mass Transfer Coefficients (m/s) [(a)] Updated Calculation from Tank Data	Previous Calculation from Tank Data[1]
No Slurry Pumps Operating	6.0E-07	4.0E-07
One Slurry Pump Operating	1.5E-06	4.2E-06
Two Slurry Pumps Operating	3.0E-06	8.0E-06

(a) The mass transfer coefficients reference a volume of 720,000 gal.

Figure 1. Tank 50H Vapor Phase Benzene Concentration

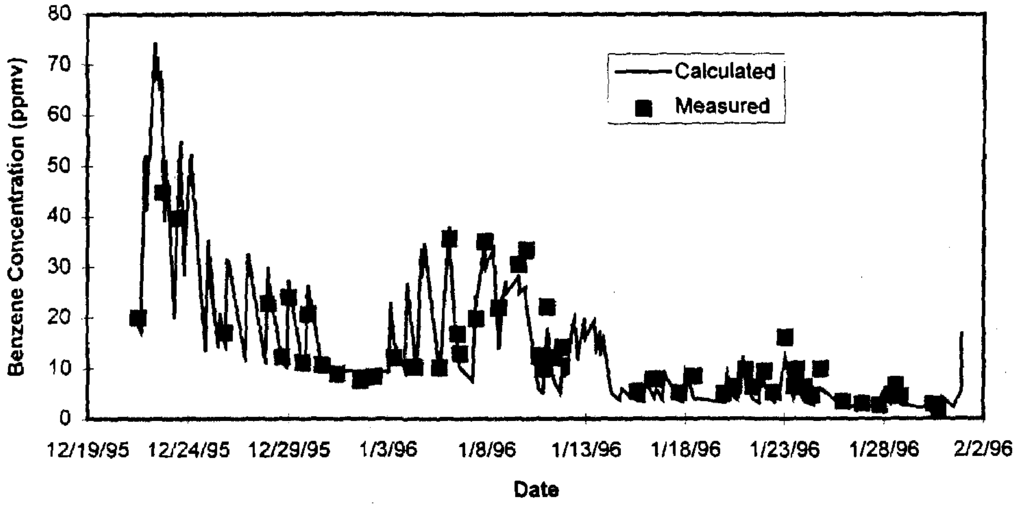


Figure 2: Calculated versus Measured Vapor Phase Benzene Concentration for Tank 50H

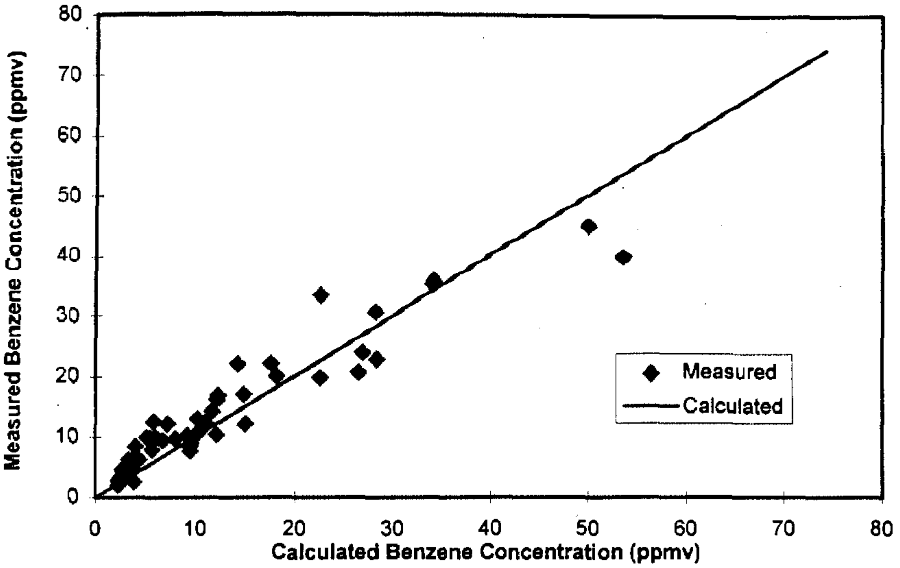
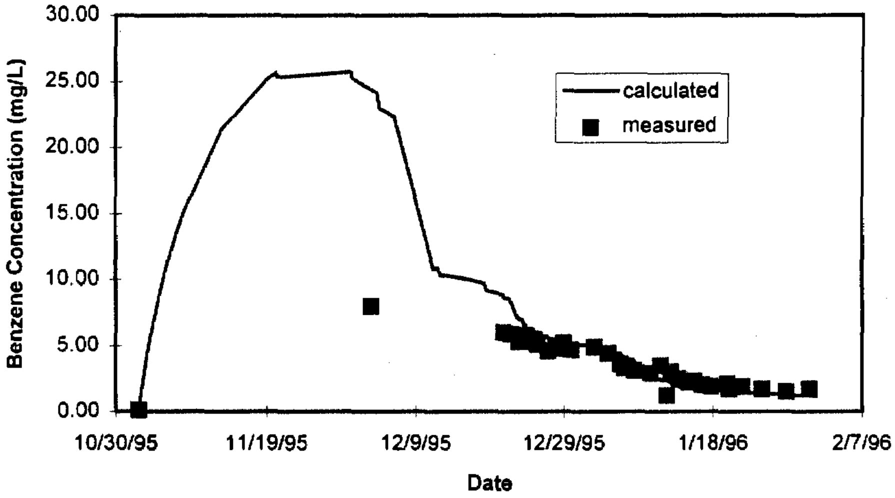


Figure 3. Tank 50H Liquid Phase Benzene Concentration



Tank 50H Estimated Bounding Mass Transfer Coefficients

Researchers used a method suggested by Kawase and Moo-Young to estimate the bounding mass transfer coefficients for Tank 50H.[5] This method derives from consideration of data for power-law Newtonian and non-Newtonian fluids in tanks with agitators. However, one may apply it to tanks with pumps of known pump horsepower. A panel of mixing consultants suggested this application: Prof. P. Peterson of the University of California-Berkeley, Prof. E. Cussler of the University of Minnesota and Dr. E. J. Lahoda of the Westinghouse Science and Technology Center, on March 24, 1997. They agreed this application should yield conservative estimates. The Kawase/Moo-Young method uses the following two equations.

$$k = 0.138\,Sc^{-2/3}\left(\nu\tilde{\varepsilon}\right)^{1/4} \text{ and} \tag{3}$$

$$\tilde{\varepsilon} = \frac{N_p N^3 D_I^5}{\left(\pi/4\right) D_T^2 H}, \tag{4}$$

where Sc = the Schmidt number (ratio of diffusivity to kinematic viscosity),
$\tilde{\varepsilon}$ = the energy dissipation per unit mass
N_P = the power number (power/(density*(rotational speed)^3*(impeller diameter)^5),
N = rotational speed of the impeller,
D_I and D_T = the diameter of the impeller and tank, respectively,
H = the liquid height in the tank and
ν = the kinematic viscosity.

The kinematic viscosity used in this method used salt solution viscosities documented in Reference 6. The diffusivity uses the Wilke-Chang correlation described in Reference 7. As indicated above, the K/M-Y method applies to stirred tanks. However, the impeller diameter and rotational speed cancel from the equation (4). Therefore, one may adapt this equation for pumped tanks. This equation would produce conservatively large mass transfer coefficients for Tank 50H, if one uses the rated power of the pumps instead of the power imparted to the liquid. To add further confidence to these numbers, Kawase and Moo-Young checked their correlation against several sets of data from other researchers. We approximate the largest standard deviation between their correlation and the data examined as 20.4%.* Researchers found that because of changes in diffusivity and kinematic viscosity, mass transfer coefficients in filtrate (5 M Na$^+$ salt solution) varied by a factor of 2.90 over a temperature range of 20 to 50 °C. The Appendix discusses the derivation of this factor in greater detail. Multiplying this factor by three times the assumed standard deviation obtained from the Kawase/Moo-Young work (1.612) gives an overall increase of a factor of 4.67. We investigated the effect of changing the contents of Tank 50H from ITP filtrate to wash water, which changes the kinematic viscosity. Table 2 gives the estimated bounding mass transfer coefficients for Tank 50H. Figure 4 plots the predictions for filtrate along with best estimate values.

Table 2. Bounding Mass Transfer Coefficients for Tank 50H

	Estimated Bounding Mass Transfer Coefficients (m/s)[(a)]	
# Pumps	**with Filtrate (~5 M Na$^+$)**	**with Wash Water (~2 M Na$^+$)**
1 Pump Operation	3.9E-05 - 6.3E-05	7.6E-05 - 1.2E-04
2 Pump Operation	4.6E-05 - 7.5E-05	9.8E-05 - 1.5E-04

(a) The range of mass transfer coefficients given reflects the range of available liquid volumes (140 to 1,000 kgal)[8]; it does not indicate the accuracy or precision of the calculations.

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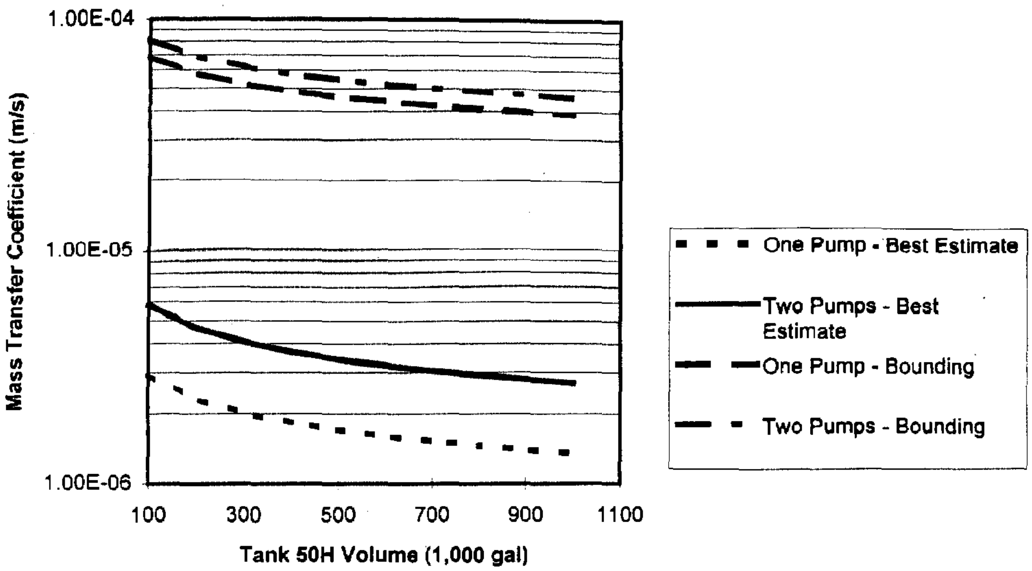
* Note that Kawase and Moo-Young give an average deviation rather than a standard deviation. Since their report does not allow determination of the standard deviation, we chose to treat the average deviation as a standard deviation. The data presented in their report fit the model well, and all of the data fall within three times the average deviation.

Figure 4. Tank 50H Filtrate Mass Transfer Coefficients as a Function of Tank Volume



Mass Transfer Coefficients for the SSHT, FWRT and LPDT

Since no data exists to calculate the mass transfer coefficients for the SSHT, FWRT and LPDT directly, researchers estimate the mass transfer coefficients for these tanks using the Kawase/Moo-Young method. Since this method derives from data for agitated tanks, it should give reasonable results for the SSHT, FWRT and LPDT. As mentioned above, the comparison by Kawase and Moo-Young of their model yielded good agreement with data obtained by other researchers.

Table 3 lists the design data used in this calculation. Note that though the impeller diameter and rotational speed appear in equations, they cancel from the solution and thus do not appear below. Also note that researchers conservatively use the rated power of the agitator motor rather than the lesser power imparted to the liquid.

Researchers determined bounding mass transfer coefficients from the best estimate values by applying the factor of 4.64 described above. Table 4 gives ranges of best estimate and bounding mass transfer coefficients. All mass transfer coefficients assume agitator operation. Mass transfer coefficients for quiescent periods should equal those given in Table 1 for Tank 50H.

Table 3. Design Information for Tanks

Tank	Volume (gal)	Pump/Agitator	Pump/Agitator Power (hp)	Tank Diameter (ft)	Reference
50H	140,000 - 1,000,000	2 pumps	150 each	84.8[(a)]	9
SSHT	8,900 - 37,000[(b)]	agitator	20	25	10
FWRT	2,080 - 5,571[(c)]	agitator	3.5	12	11
LPDT	760 - 7,125[(d)]	agitator	5	8	12,13

(a) The diameter of Tank 50H corrected to account for the center column.

(b) Physical limits for the SSHT run from virtually empty to a volume of 50,390 gal. The agitator shuts down at volumes below 8,900 gal. An administrative upper limit exists at 37,000 gal. A high level alarm exists at 47,300 gal.

(c) Physical limits for the FWRT run from virtually empty to a volume of 6,500 gal. An administrative upper limit exists at 3,900 gal. A high level alarm exists at 5,571 gal.

(d) The minimum volume given for the LPDT represents the low volume cutoff to prevent pump cavitation. The high volume reflects the high volume alarm point. An overflow volume exists at a volume of 7,790 gal.

Table 4. Estimated Mass Transfer Coefficients for the SSHT, FWRT and LPDT

Tank	Volumes Assumed (gal)	Mass Transfer Coefficient (m/s)[(a)] Best Estimate	Bounding Estimate
SSHT	8,900 - 37,000	1.1E-05 - 1.6E-05	5.3E-05 - 7.6E-05
FWRT	2,080 - 5,571	1.2E-05 - 1.5E-05	5.5E-05 - 7.0E-05
LPDT	760 - 7,125	1.2E-05 - 2.1E-05	5.4E-05 - 9.9E-05

(a) The range of mass transfer coefficients accommodates the range of likely liquid volumes; it does not indicate the accuracy or precision of the calculations.

Effects of Surfactants on Benzene Mass Transfer Coefficients

Several different surfactants find use in the High Level Waste processing and could reach Tank 50H, SSHT, the FWRT and the LPDT. Previous testing of the effects of these surfactants on mass transfer of benzene provides some insight. Since ITP adds tri-n-butyl phosphate (TBP) to control foaming in the benzene stripper columns, TBP poses the primary concern. Testing at Koch indicated the high concentrations of TBP (>300 ppm) reduces stripping efficiency in the ITP benzene stripper.[14] Though the method of benzene removal in the stripper differs from that in the tanks, this data indicate the mass transfer coefficients decreases if significant concentrations of TBP occur in any of the tanks. Though high concentrations of Surfynol™104E reduced the rate of benzene removal in sparging tests,[15] low concentrations showed no effect on benzene removal rate.[16] Therefore low concentrations of Surfynol should not affect the benzene mass transfer coefficients.

Uncertainties in Mass Transfer Coefficient Calculations

The mass transfer coefficients calculations documented in this report have considerable uncertainty. For the Tank 50H calculations, sparse measurements of vapor and liquid benzene concentration exist with considerable uncertainty in the benzene concentration measurements (>10%). Benzene concentration, particularly in the vapor phase, depends highly on the pump operation status at the time of sampling. However, times for sampling and pump operation remain uncertain. Because of the very few samples taken, the data do not show the relatively rapid changes in the vapor phase benzene concentration that can occur with changes in pump operation. Researchers assumed mass transfer coefficients for Tank 50H act independently of temperature. Under the small range of temperatures studied (27 - 35 °C), one should expect only small changes in mass transfer.

The calculations assume benzene generated from the decomposition of each mole of triphenylboron into three moles of benzene. The process actually includes intermediates of diphenylborinic acid and phenylboric acid. The calculations ignore these intermediates because their decomposition appears rapid compared to that of triphenylboron. The calculations account for change in decomposition with changing temperature, but our knowledge of the production of benzene from tetraphenylborate and its decomposition products remains incomplete.

Tank 50H currently acts as a holding tank for In-Tank Precipitation filtrate before transfer to Saltstone. The filtrate has a Na^+ concentration of about 5 M. In the future, Tank 50H will serve as a wash water hold tank, and the sodium concentration will be about 2.2 M. The mass transfer coefficients change with the change in sodium concentration, primarily as function of changes in viscosity. The bounding estimates include these changes for Tank 50H. One would expect a similar effect on best estimate numbers.

The Kawase/Moo-Young model for estimating mass transfer coefficients provides an empirical fit to data obtained in laboratory scale tests. Kawase and Moo-Young checked the data from other researchers in systems where oxygen or carbon dioxide absorbed into water and other aqueous solutions exhibiting various rheological behavior. The model gave good agreement with the experimental results in all cases referenced. We use this model to examine benzene stripped from ITP filtrate. We assumed that benzene, a volatile organic liquid, would behave similarly to oxygen and carbon dioxide in aqueous systems and that the mass transfer coefficient for absorption equates to that for stripping. The model also lacks comparison with full-scale tanks. We used the rated power of agitators and pumps in our calculations instead of the power imparted to the liquid. This assumption should give larger mass transfer coefficients. Additionally, it is assumed that agitators are more efficient than pumps in mixing tanks, and therefore the K/M-Y model should be even more conservative for tanks mixed by pumps, such as Tank 50H, than for tanks mixed by agitator. We compared estimated Tank 50H mass transfer coefficients calculated using the Kawase/Moo-Young model to the mass transfer coefficients derived from Tank 50H data. The Kawase/Moo-Young mass transfer coefficients proved as much as an order of magnitude greater than those derived from data. This indicates that the Kawase/Moo-Young model should provide conservative estimates for Tank 50H.

Path Forward

The calculations and data given in this report benefited from a discussion with a panel of mixing experts: Prof. E. Cussler, Prof. P. Peterson and Dr. E. J. Lahoda. They thought the best estimate values presented in this report reasonable and the bounding values conservative. They recommended future efforts include a literature search to find mass transfer models which might better model ITP and Saltstone tanks. They further suggested that we limit testing, if any, solely to that needed to verify the effect of various parameters on mass transfer coefficients in any models used.

A subsequent report will address recommendations on conduct of tests in Tank 50H and the Saltstone tanks to verify benzene mass transfer. A second report will more fully document the method used to regress mass transfer coefficients from tank data.

REFERENCES

1. R. A. Peterson, C. L. Crawford and R. F. Swingle, "Initial Estimates of Mass Transfer Coefficients in Tank 48H and Tank 50H (U)", WSRC-TR-96-256, Revision 0, August 16, 1996.

2. A. W. Wiggins, "Estimate Bounding MTCs for ITP Tanks and Provide Plans for Plant Tests (U)", HLE-TTR-97019, Revision 0, November 15, 1996.

3. D. D. Walker, "Vapor Pressure of Benzene, Methanol, and Isopropanol Over Salt Solutions (U)", DPST-88-661, March 28, 1989.

4. C. L. Crawford and R. A. Peterson, "Decomposition Studies of Triphenylboron, Diphenylborinic Acid and Phenylboric Acid in Aqueous Alkaline Solutions Containing Copper (U)", WSRC-TR-97-0045, Revision 0, February 7, 1997.

5. Y. Kawase and M. Moo-Young, "Mass Transfer at a Free Surface in Stirred Tank Bioreactors", Chemical Engineering Research and Design, March 1990, Vol. 62, No. 2, pp. 189-194.

6. D. D. Walker and G. K. Georgeton, "Viscosity and Density of Simulated Salt Solutions (U)", WSRC-RP-89-1088, October 19, 1989.

7. C. J. King, Separation Processes, 2nd Edition, New York: McGraw-Hill Book Company, 1980, pp. 513-514.

8. P. L. Rutland, e-mail to R. F. Swingle, "Re: Anticipated Tank 50H Operation", March 20, 1997.

9. Drawing W841273, Revision 6, "Tank 50 Waste Storage Facility Motor Schm., Sheet 1", August 16, 1996.

10. B. K. Taylor and E. J. Freed, "Engineering Position: Salt Solution Hold Tank Evaporation Cycle (U)", OPS-DTZ-96-049, October 15, 1996.

11. Telecon with B. K. Taylor, February 11, 1996.

12. Drawing 13239-MT-21214-4(1)-5, Revision 3, October, 1985.

13. Drawing W775551, Revision 14, "Low Point Drain Tank, Piping and Instrument Drawing", April 7, 1995.

14. R. F. Swingle and D. D. Walker, "Post-Mortem report on October 1993 Benzene Stripper Acceptance Testing (U)", WSRC-RP-94-574, Revision 0, June 23, 1994.

15. J. McGlynn, Notebook WSRC-NB-92-145, March 30, 1992, pp. 50-70,

16. M. A. Baich, "Qualification of Data: 1/200th Scale SRAT Late Wash Permeate Sparging (U)", WSRC-RP-93-229, January 20, 1993.

ACKNOWLEDGEMENTS

The authors thank Dr. Per Peterson of the University of California at Berkeley for his recommendation of Reference 5 giving a correlation for estimation of mass transfer coefficients. We also thank Blaine Taylor, Maria Rios-Armstrong and Ken Sibley of High Level Waste Engineering for providing tank design information used in this report.

APPROVALS

Charles A. Nash Date: 6/16/97
C. A. Nash, Design Check per Manual E7, Procedure 2.40
Waste Processing Technology

Samuel D. Fink Date: 6-16-97
S. D. Fink, Manager, Manager,
Liquid Waste Processing

M. J. Montini Date: 6-19-97
M. J. Montini, Deputy Manager
ITP/ESP Engineering

Date: 7/24/97
J. T. Carter, ITP Flow-Sheet Task Team

THE 71 KJ/MOLE USED IN THIS ANALYSIS IS NOT CORRECT PER REF. 4. THIS ERROR WILL BE CORRECTED IN FUTURE UPDATES OF THE MASS TRANSFER COEFFICIENTS BASED ON TANK MEASUREMENTS. JTC
7/24/97

APPENDIX

Derivation of the Ratio Between the Mass Transfer Coefficients at 20 °C and 50 °C

The Kawase/Moo-Young method uses the following two equations.

$$k = 0.138\, Sc^{-2/3} (\nu \tilde{\varepsilon})^{1/4} \text{ and} \tag{1}$$

$$\tilde{\varepsilon} = \frac{N_p N^3 D_I^5}{\left(\pi/4\right) D_T^2 H}, \tag{2}$$

where Sc = the Schmidt number (ratio of diffusivity to kinematic viscosity),
$\tilde{\varepsilon}$ = the energy dissipation per unit mass
N_P = the power number (power/(density*(rotational speed)^3*(impeller diameter)^5),
N = rotational speed of the impeller,
D_I and D_T = the diameter of the impeller and tank, respectively,
H = the liquid height in the tank and
ν = the kinematic viscosity.

The kinematic viscosity includes salt solution viscosities documented in Reference 6. The diffusivity uses the Wilke-Chang correlation, for binary systems, given below.[7]

$$D_{AB} = 7.4 \times 10^{-12} \frac{(\phi M_B)^{0.5} T}{\mu_B V_A^{0.6}} \tag{3}$$

where ϕ = association parameter for the solvent (2.6 for water),
M_B = Molecular weight of the solvent (18 for water),
T = the solution temperature in Kelvin,
μ_B = the viscosity of the solvent in centipoise and
V_A = the molal volume of pure solute at the normal boiling point (mL/mole - this was derived from 0.879 g/mL, the density of benzene at 20 °C).

Researchers did not account for the multicomponent nature or high ionic strength of the system. The current state-of-the-art for this topic does not provide extensively tested correlations for such systems. Researchers examined the change in mass transfer coefficients between 20 and 50 °C. Previous work provides viscosity data for 5 M Na^+ salt solution (average OH^-) for three temperatures between 24 and 35.1 °C.[6] The authors used these data to produce an equation for viscosity with respect to temperature for 5 M Na^+ salt solution by linear regression. They then calculated viscosities for 20 and 50 °C and used to calculate diffusivities, kinematic viscosities and then mass transfer coefficients for 5 M Na^+ salt solution with all other variables held constant in the Kawase/Moo-Young equation. This approach provides a ratio of the mass transfer coefficients at the two temperatures of 2.90. To check whether a lower sodium molarity salt solution falls within this ratio, the authors used this procedure to calculate the ratio for benzene in water, producing a value of 2.05. Therefore it appears that the 5 M Na^+ ratio addresses wash water (~2 M Na^+).

Distribution

D. B. Amerine, 719-4A
M. J. Barnes, 773-A
T. E. Britt, 732-B
J. T. Carter, 704-25S
G. L. Cauthen, 241-119H
N. F. Chapman, 704-Z
W. C. Clark, 704-56H
C. L. Crawford, 773-41A
S. J. Eberlein, 704-56H
H. H. Elder, 704-S
S. D. Fink, 773-A
T. J. Fiske, 241-120H
J. R. Fowler, 704-Z
E. J. Freed, 704-Z
M. S. Hay, 773-A
M. J. Hitchler, 992W-1
D. T. Hobbs, 773-A
R. A. Jacobs, 704-T
M. D. Johnson, 704-56H
M. T. Keefer, 704-56H
J. C. King, 241-120H
T. J. Lex, 719-4A
B. L. Lewis, 703-H
J. C. Marek, 704-T
J. D. Menna, 730-2B
M. S. Miller, 704-56H
M. J. Montini, 704-56H
J. P. Morin, 719-4A
C. A. Nash, 773-43A
J. K. Norkus, 730-2B
L. M. Papouchado, 773-A
R. A. Peterson, 773-A
S. F. Piccolo, 704-56H
M. R. Poirier, 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
B. K. Taylor, 704-Z
G. A. Taylor, 703-H
T. C. Temple, 703-H
J. K. Thomas, 730-2B
W. B. Van Pelt, 676-1T
D. D. Walker, 773-A
W. R. Wilmarth, 773-42A
A. W. Wiggins, 241-152H
G. T. Wright, 773-A
LWP Files c/o A. Patterson, 773-A
ITP Files c/o L. Sumner, 704-56H
TIM, 703-43A

WSRC-TR-97-0167

97/2509

Confidence Limits for Mass Transfer Coefficients for Benzene Release From Tank 48H and 49H (U)

R. A. Peterson R.A. Pete

Publication Date: June 16, 1997

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ADC &
Reviewing
Official: Samuel D. Fink
Samuel D. Fink, Group Mgr
(Name and Title)
Date: 7-23-97

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SUMMARY

This document provides confidence limits for the mass transfer coefficients for benzene release from Tanks 48H and 49H. The analysis performed in development of this document leads to the following observations.

- Under conditions of low benzene inventories or frequent pump operations, mass transfer coefficients for Tank 48H should range from 0.5 to 1.3 x10^{-5} m/s. These values have an upper 95% confidence limit of 7.8 x 10^{-5} m/s.

- Under conditions of low benzene inventories or frequent pump operations, good agreement exists between measured Tank 48H mass transfer coefficients and those estimated using published correlation from Kawase and Moo-Young.

- Under conditions of low benzene inventories or frequent pump operations, mass transfer coefficients for Tank 49H should range from 1.0 to 2.7 x10^{-5} m/s with an upper 95% confidence limit of 8.4 x 10^{-5} m/s.

- At least one benzene release event from Tank 48H (on March 5 of 1996) proves inconsistent with the proposed mechanism for benzene release. However, the measured release rate agrees with the evaporation of a small (20 kg) amount of benzene at the slurry surface.

INTRODUCTION

Starting in September 1995, tetraphenylborate decomposed in Tank 48H to produce benzene. Between September 1995 and the present, In Tank Precipitation (ITP) personnel operated the mixing pumps in Tank 48H to remove this benzene. High Level Waste Engineering requested that the Waste Processing Technology Section analyze a limited number of these benzene release events to provide an estimate of, and a conservative limit for, the mass transfer coefficients for subsequent benzene releases from both Tank 48H and Tank 49H.[1] This document provides that analysis.

DISCUSSION

Tank 48H Mass Transfer Coefficients

One method to estimate mass transfer coefficients for the release of benzene from the tanks involves analysis of existing data gathered during the release. More than 80 measurements of benzene release following the start of pump operations occurred in Tank 48H between October 1995 and July 1996. These measurements span from immediately after completion of sodium tetraphenylborate addition to the tank in September of 1995 until effectively complete depletion of the benzene inventory in the tank. During this time frame, the benzene concentration in Tank 48H ranged from trace levels to well in excess of the salt solution solubility limit. Previously, researchers defined criteria for these release events that ensure the accuracy of derived mass transfer coefficients and ensures the ability to obtain these values from the measurements.[2] These criteria require significant depletion of the benzene inventory during the duration of the specified continuous pump operation. Significantly depleted means a decrease by 50% from the maximum benzene release rate. This requirement arises from the need to estimate the initial benzene concentration in the slurry prior to pump operations. Without this estimate of initial benzene inventory, one can not separate the impact of the mass transfer coefficient and the initial concentration[4] to provide an upper confidence limit on the mass transfer coefficient.

To date, only one of the more than 80 documented release events meets this criteria. In November of 1995, ITP personnel collected data during pump operations (frequently denoted Slurry Pump Bump Test #3).[3] This operation met the specified criteria for mass transfer analysis. Previously, researchers analyzed Slurry Pump Bump Test #3 to provide an estimate and confidence limits on the mass transfer coefficient observed during that operation.[4] Based on the conditions of Slurry Pump Bump Test #3, the mass transfer coefficient fell between 1.5 and 2.6 $\times 10^{-5}$ m/s with a best estimate value of 1.9×10^{-5} m/s. At that time, Tank 48H contained approximately 160,000 gallons of 3 wt% slurry.

As indicated above, data exist only at a limited number of conditions that allow estimation of mass transfer coefficients for Tank 48H. To provide a check of the validity of these measurements and to provide a rationale for estimating mass transfer coefficients at conditions other than those tested, researchers identified a theoretical model for mass transfer coefficients.[i] This model expresses the mass transfer coefficient as a function of a number of slurry and tank parameters:

$$k = 0.138\, Sc^{-2/3} (\nu\tilde{\varepsilon})^{1/4} \qquad 1$$

where
Sc is the Schmidt number (ν/D_{AB})
ν is the kinematic consistency[6,7]
D_{AB} is the diffusivity of benzene in salt solution[5]
and
$\tilde{\varepsilon}$ is the energy dissipation rate per unit mass

The Schmidt number and kinematic consistency depend on the slurry consistency and slurry density.

As indicated by the presence of the Schmidt number in this correlation, Equation 1 assumes diffusion of benzene through a depleted layer near the slurry-vapor interface controls the mass transfer. The mathematical development employed to produce Equation 1 focused primarily with developing an estimate of the impact of pump operations (and other parameters) on the depth of this surface layer.

Other researchers previously measured the dependence of slurry consistency and slurry density for this Bingham plastic material on weight percent solids and salt concentration.[6,7] Using these values and an average pump energy dissipation of 125 hp, one may estimate a mass transfer coefficient at the Tank 48H conditions during Slurry Pump Bump Test #3. This calculation provides an estimate of 1.8×10^{-5} m/s, in good agreement with the value regressed from measurements. Similarly, one can then use Equation 1 to estimate mass transfer coefficients for Tank 48H at conditions other than those tested. Figure 1 and Table 1 provide such estimates at a variety of conditions. Appendix A contains the information required to generate this table with the exception of the energy dissipation rate.

Previously, researchers developed a factor to apply for the Kawase and Moo-Young value to obtain a 95% confidence limit on the mass transfer coefficients.[8] That factor included a multiplier to reflect the maximal expected variance of the predicted coefficients from Equation 1 from the literature data for numerous systems. Another multiplier corrected for compositional and thermal variances. For the application to slurries in Tanks 48H and 49H, a single multiplier does not cover all cases.

The estimates of mass transfer coefficients in Figure 1 assume slurry at ambient temperature and 5 molar sodium (i.e., unwashed). Development of upper confidence limits must consider temperature and precipitate washing. For slurries containing less than 3 wt % solids, washing will produce a decrease in the slurry viscosity. However, for system containing more than 3 wt % solids, experimental evidence indicates that washing does not significantly impact the slurry consistency.[6] However, washing also decreases the solution density. Furthermore, in estimating the possible changes in mass transfer coefficients for changes in temperature and washing, it is necessary to also consider changes in diffusivity. The diffusivity of benzene in salt solution will increase with increasing temperature and with decrease in solution molarity. Thus, while the kinematic

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[i] Y. Kawase and M. Moo-Young, "Mass Transfer at a Free Surface in Stirred Tank Bioreactors", Trans IChemE, Vol. 68, p. 189, March 1990.

consistency increases with washing in some cases, the Schmidt number decreases significantly in all cases for washed material, and thus, the limiting conditions should employ washed material.

Note that the facility constrains operations to a maximum anticipated temperature in Tank 48H of 45 °C. Increasing temperature to 45 °C will produce a decrease in the viscosity of slurries containing less than 3 wt % solids. No measurements exist regarding the impact of heating slurries containing higher concentration of solids. However, since solid content dominates the value of consistency, thermal variance should prove minimal especially for more concentrated slurries. However, a conservative estimate assumes the consistency change for slurries containing higher solids contents equals that change for slurries containing lower solids.

Figure 2 and Table 1 provide values for these upper confidence limit estimates based on the conservative slurry conditions at a variety of tank conditions. Table 1 provides upper confidence limits and estimated mass transfer coefficients at stages indicative of typical plant operations.

Figure 1. Estimated Tank 48H Benzene Mass Transfer Coefficients for 4 Pumps (KMY)

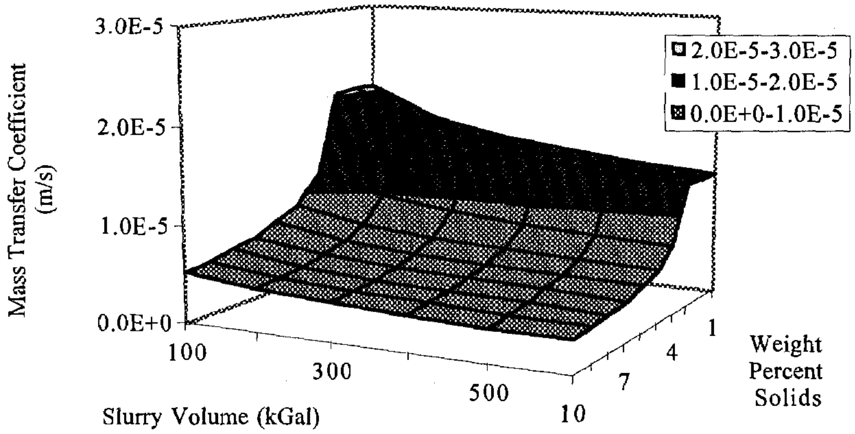


Figure 2. Upper Confidence Limit for Tank 48H Benzene Mass Transfer Coefficient for 4 Pumps (KMY)

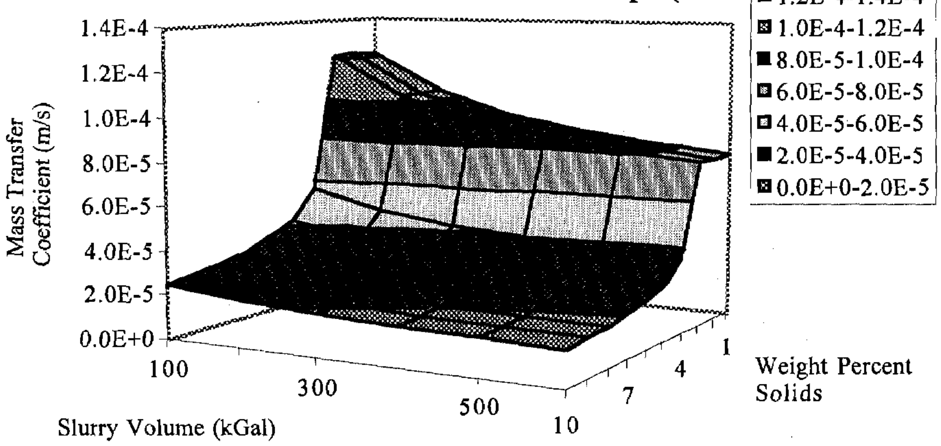


Table 1. Estimated and confidence limit mass transfer coefficients for Tank 48H with 4 pumps operating.

	Weight Percent Solid	Tank Level (kGal)	Mass Transfer Coefficients	
			Estimated at ambient conditions (10^{-5}m/s)	95 % Confidence Limit at limiting conditions (10^{-5}m/s)
Start of typical 1st batch	1.0	600	1.3	7.8
End of typical 1st batch	4.0	150	1.0	5.0
Start of typical 2nd batch	1.8	600	1.3	7.8
End of typical 2nd batch	7.0	150	0.6	2.9
Start of typical 3rd batch	2.5	600	1.3	7.8
End of typical 3rd batch	10.0	150	0.5	2.3

Note that these and all other estimates provided in this document apply to the operation of four pumps. Equation 1 can provide an estimate of the impact of decreasing the number of pumps employed. This estimate results in the following correction for decreasing the number of pumps employed

$$k_N = k_4\left(\frac{N}{4}\right)^{1/4} \qquad 2$$

where k_N represents the mass transfer coefficient for N ($N \le 4$) pumps and k_4 denotes the mass transfer coefficient for four pumps shown in the appropriate figure or table. Note that releases from Tank 48H appear consistent with this correlation for two and three pumps. However, this correlation likely over predicts the mass transfer coefficient for one pump. Researchers anticipate that one pump will not adequately mix the whole of the tank contents (an assumption employed in the proposed model). This incomplete mixing becomes most evident when using only one pump and will probably result in lower than estimated mass transfer coefficients. At this time, the author can not quantify the uncertainty in the mass transfer coefficient associated with incomplete mixing of the tank contents.

As indicated previously, personnel monitored more than 80 separate instances of benzene release following initiation of pump operations in Tank 48H. While the author can not provide confidence limits for mass transfer coefficients based on the pump operations, one may evaluate these release events in light of Equation 1. Using approximate estimates of the initial benzene inventory (in particular, assuming a saturated salt solution for most of the operations of interest), all but one of the pump operations of interest fall within the mass transfer coefficients provided in Equation 1. The one event not bounded by Equation 1 involved a benzene release from Tank 48H observed on March 5, 1996. Note that while all other pump operations agree with Equation 1, not all operations provided as good agreement as Pump Bump Test #3. In particular, Equation 1 appears to overestimate by as much as 100 % the mass transfer coefficients for conditions involving 2 or fewer pumps and involving higher (>300,000 gal) tank levels. Note also that Equation 1 does not differentiate for the location of pumps. However, for operations involving only 2 pumps, the configuration of the pumps employed (i.e., adjacent vs. opposite) may significantly impact the mass transfer coefficient. A previous report specifies conditions to illuminate this difference during future pump operations.[2]

Using the upper confidence limit, researchers determined the maximum benzene release rate between November of 1995 and April of 1996 from this surface renewal model estimate of 400 g/min. However, on March 5th of 1996, facility personnel measured a release rate of approximately 1400 g/min in Tank 48H.[ii] This higher release rate suggests benzene released from Tank 48H during this time frame by a more efficient mechanism. Where the proposed model suggests benzene moves to the surface of the slurry through a diffusive mechanism, this release event appears to reflect convective transport of the benzene molecules to the slurry surface. Under such conditions, the rate of release would derive from a combination of this rate of transport and the rate of evaporation of this benzene from the slurry surface. Currently, insufficient data exists to provide an estimate of the convective transport of this material directly to the surface. However, one may provide an upper limit on the benzene release rate for this mechanism by studying the rate of evaporation. Thus, the highest achievable benzene release rate for Tank 48H of 1632 g/min[9] represents the evaporation of benzene in contact with the tank vapor space. Using that rate suggests that the March 5th release reflects the rapid convective transport and evaporation of a small quantity of benzene (~ 20 kg)[ii] at the slurry surface.

Tank 49H Mass Transfer Coefficients

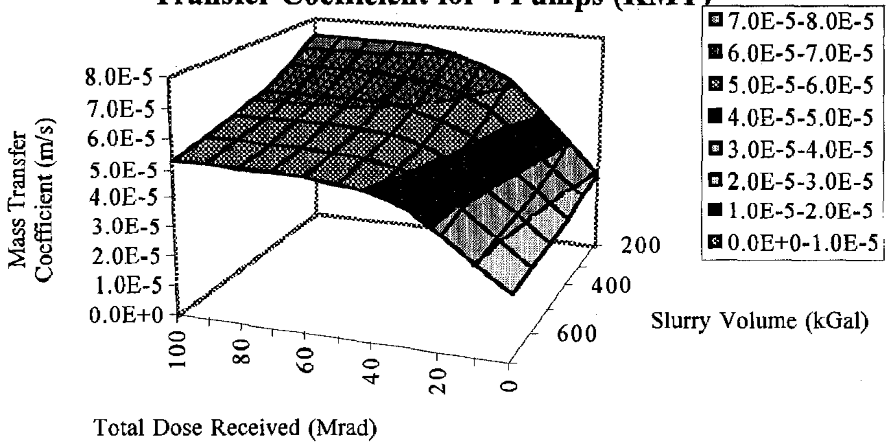
Previously, researchers suggested methods to measure mass transfer coefficients for Tank 49H.[10] To date, no measurements exist for Tank 49H to provide estimates of these mass transfer coefficients. Equation 1 provides a means to estimate the upper confidence limit on surface renewal mass transfer coefficients in Tank 49H. Figure 3 and Table 2 provide these values. The mass transfer coefficients presented in Table 2 are for 10 wt % slurry. Additional information required to generate the values presented in Table 2 are presented in Appendix A. Note that adsorbed radiation dose decreases the consistency of tetraphenylborate slurries[11] and will cause increases in the mass transfer coefficient. Note that although measurements do not exist for Tank 49H, the ability of Equation 1 to bound more than 80 pump operations in Tank 48H and the similarities between Tank 48H and 49H suggests Equation 1 will provide a reasonable estimate of mass transfer coefficients for Tank 49H. However, measurements of benzene release should occur in Tank 49H during the remainder of Cycle 1 to verify these estimates.

Table 2. Estimated and confidence limit mass transfer coefficients for Tank 49H with 4 pumps operating.

	Dose Received (Mrad)	Tank Level (kGal)	Mass Transfer Coefficients: Estimated at ambient conditions (10^{-5}m/s)	Mass Transfer Coefficients: 95% Confidence Limit at limiting conditions (10^{-5}m/s)
Start of Cycle 2	0	200	1.0	3.0
End of Cycle 2	70	110	2.8	8.4
Start of Cycle 3	30	270	1.9	5.7
End of Cycle 3	100	150	2.6	7.8
Start of Cycle 4	60	300	2.2	6.5

[ii] P. F. Peterson and E. L. Cussler, "Report on October 7 Meeting on Benzene Mass Transfer Information for ITP and Late Wash", October 14, 1996.

Figure 3. Upper Confidence Limit for Tank 49H Benzene Mass Transfer Coefficient for 4 Pumps (KMY)



CONCLUSIONS

The author estimated mass transfer coefficients for both Tank 48H and Tank 49H. These estimates assume a surface renewal model developed by Kawase and Moo-Young. Under normal operating conditions, this model provides accurate estimates of the mass transfer coefficients measured in Tank 48H. In addition, the model may provide an upper confidence limit on the mass transfer coefficients for these two tanks. However, on March 5 of 1996, a benzene release event occurred in Tank 48H that exceeded even the 95% confidence estimate from the surface renewal mechanism for release of benzene from this tank. The data collected during this event suggests the evaporation of a small (~ 20 kg) quantity of benzene above the slurry surface upon agitation of the tank.

Appendix A. Physical values for various tank conditions

Table A.1. Conditions Employed in Figures 1 and 2 and Table 1 for Tank 48H. Data provided for each slurry concentration employed in Table 1.

Anticipated Conditions		Limiting Conditions	
Temperature:	25 °C	Temperature	45 °C
Salt Concentration:	5.0 M	Salt Concentration:	0.2 M
Density^7:	1.23 g/cm^3	Density^7:	1.02 g/cm^3
Diffusivity^5:	0.47x10^{-5} cm^2/s	Diffusivity^5:	1.7x10^{-5} cm^2/s

wt % Solid	μ (cP) [Ref 6]	ν (cm^2/s)	Sc	μ (cP) [Ref 6]	ν (cm^2/s)	Sc
1	2	0.0162	3455	0.60	0.0059	353
1.8	2	0.0162	3455	0.60	0.0059	353
2.5	2	0.0162	3455	0.60	0.0059	353
4	7.8	0.0633	13474	3.90	0.0383	2294
7	29.7	0.2411	51304	14.85	0.1459	8736
10	51.6	0.4189	89135	25.80	0.2535	15177

Table A.2. Conditions Employed in Figure 3 and Table 2 for Tank 49H (assuming 10 wt% slurry). Data provided for each applied dose employed in Table 2.

Anticipated Conditions		Limiting Conditions	
Temperature:	25 °C	Temperature	45 °C
Salt Concentration:	0.2 M	Salt Concentration:	0.2 M
Density^7:	1.02 g/cm^3	Density^7:	1.02 g/cm^3
Diffusivity^5:	1.0x10^{-5} cm^2/s	Diffusivity^5:	1.7x10^{-5} cm^2/s

Dose (Mrad)	μ (cP) [Ref 6]	ν (cm^2/s)	Sc	μ (cP) [Ref 6]	ν (cm^2/s)	Sc
0	26.0	0.255	25543	13.00	0.128	7647
30	4.6	0.045	4512	2.30	0.023	1351
60	3.1	0.031	3056	1.56	0.015	915
70	3.0	0.030	2992	1.52	0.015	896
100	3.0	0.030	2950	1.50	0.015	883

Note: for limiting and Tank 49H employing of 0.2 M salt concentration, viscosity of the supernate is taken to be that of water.

APPROVALS

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INTERNAL REFERENCES - NOT TO BE INCLUDED FOR PUBLIC DISTRIBUTION

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[1] J.E. Marra and J.T. Carter, "Estimate Bounding MTCs for ITP Tanks and Provide Plans for Plant Tests (U)", HLE-TTR-97019, Revision 0, November 15, 1996.

[2] R.A. Peterson, "Proposed Tank 48H Pump Operation During Cycle 1 (U)", WSRC-RP-97-219, March 26, 1997.

[3] O.Carona-Quiles, J.L. Kelly, M.R. Williams and D.A. Zupon, "Quick-Look Plots for SP-95-ITP-014 Slurry Pump Bump Test #3", HLW-ITP-950647, November 30, 1995

[4] R. A. Peterson, C. L. Crawford and R. F. Swingle, "Initial Estimates of Mass Transfer Coefficients in Tank 48H and Tank 50H (U)", WSRC-TR-96-256, Revision 0, August 16, 1996.

[5] C.J. King, Separation Processes, 2nd Edition, New York: McGraw-Hill Book Company, 1980, pp. 513-514.

[6] M. A. McLain and I. D. Goren, "Rheology of Non-Radioactive Simulant of Concentrated Tetraphenylborate Precipitate", DPST-84-401, March 30, 1984.

[7] D. D. Walker and G. K. Georgeton, "Consistency and Density of Simulated Salt Solutions (U)", WSRC-RP-89-1088, October 19, 1989.

[8] R. F. Swingle, R. A. Peterson and M. R. Poirier, "Updated Estimates of Mass Transfer Coefficients in Tank 50H, Salt Solution Hold Tank, Flush Water Receipt Tank and Low Point Drain Tank (U)", WSRC-TR-97-0056, April 11, 1997.

[9] J.K. Norkus, "Release from a free benzene layer in ITP Tank 48", M-CLC-H-01350, September 3, 1996.

[10] R. A. Peterson, "Proposed Tank 49H Pump Operation During Cycle 1 (U)", WSRC-RP-97-377, May 1997.

[11] D.D. Walker and J.P. Doherty, "The Effects of Gamma Irradiation on the Rheology of KTPB Slurries", DPST-85-926, November 5, 1985.

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Estimates of Mass Transfer Coefficients in Tank 50H and 48H (U)

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SUMMARY

The authors developed methods to estimate mass transfer coefficients for Tank 50H and 48H using measurements from the vessels. The following table describes the steps employed in these methods.

Step to be completed	Tank 50H	Tank 48H
Obtain data from tank	Periodic liquid and vapor samples analyzed	On line GC, temperature and ventilation rate measurements
Specify Input Parameters	2 pump mass transfer coefficient 1 pump mass transfer coefficient 0 pump mass transfer coefficient Initial Triphenylborane concentration Triphenylborane decomposition rate constant	4 pump mass transfer coefficient 25 °C benzene generation rate Initial liquid benzene concentration
Evaluate Error Function	Analytically	Numerically
Minimize Error Function for all variables simultaneously	Microsoft© Excel Solver	FORTRAN Subroutine
Evaluate Confidence Limits	Microsoft© Excel Solver	FORTRAN Subroutine

Applying these methods, mass transfer coefficients (k, with subscript representing the number of pumps operating) were estimated for 0, 1 or 2 pumps in Tank 50H and for 4 pumps in Tank 48H.

For Tank 50H containing 720,000 gallons of solution, the authors estimated the mass transfer coefficients as

$$k_0 = 2.6\text{x}10^{-7} \text{ m/s}$$
$$k_1 = 9.7\text{x}10^{-7} \text{ m/s}$$
$$k_2 = 1.5\text{x}10^{-6} \text{ m/s}$$

for 0, 1, and 2 pumps, respectively, with 95% confidence limits for k_0 between 2.0×10^{-7} and 3.5×10^{-7}, k_1 between 0.5 $\text{x}10^{-6}$ and 1.6 $\text{x}10^{-6}$ m/s and k_2 between 1.2 $\text{x}10^{-6}$ and 2.0 $\text{x}10^{-6}$.

For Tank 48H containing 167,000 gallons of 3 wt % slurry, the analysis yields a mass transfer coefficient for four pumps of

$$k_4 = 4.0 \text{ x}10^{-6} \text{ m/s}$$

with 95% confidence limits between 3.0 $\text{x}10^{-6}$ and 5.5 $\text{x}10^{-6}$ m/s. All of these estimates are highly dependent on the assumptions used in their development, in particular upon the Henry's law coefficient and upon the form of the generation rate.

INTRODUCTION

Starting in September 1995, tetraphenylborate and its decomposition products decomposed in Tank 48H and Tank 50H to produce benzene. Between September 1995 and the present, In-Tank Precipitation (ITP) personnel operated the mixing pumps in Tank 48H and Tank 50H to remove this benzene. High Level Waste Engineering requested that the Waste Processing

Technology Section analyze a limited number of these benzene release events to provide an estimate of the mass transfer coefficients for these benzene releases from both Tank 48H and Tank 50H.[1] This document provides that analysis.

DISCUSSION

Approach

From September of 1995 through January of 1996, ITP personnel made periodic measurements of the temperature, tank level, liquid phase benzene concentration and vapor space benzene concentration in Tanks 48H and 50H. In addition, personnel periodically recorded the ventilation rate in Tank 48H. This document will illustrate use of those measurements to provide estimates of the mass transfer coefficients for benzene release from the tank.

Theory

The following two differential equations describe the mass transfer of semi-soluble species from the aqueous phase to the vapor phase for a ventilated tank.

$$\frac{dy}{dt}=\frac{kA(m(x)-y)-yQ(t)}{V_y}, \qquad 1$$

$$\frac{dx}{dt}=\frac{G(t)-kA(m(x)-y)}{V_x}, \qquad 2$$

In these equations, x denotes the concentration of benzene in the liquid phase, y gives the concentration of benzene in the vapor phase, k represents the mass transfer coefficient, and A gives the surface area available for mass transfer. Similarly, $m(x)$ represents the vapor liquid equilibrium expression, Q gives the ventilation rate, V_y denotes the vapor space volume in the tank, V_x signifies the volume of the liquid in the tank, and $G(t)$ gives the benzene generation rate.

Solving this set of differential equations requires values (or functional expressions) for the generation rate, mass transfer coefficient, vapor liquid equilibrium, surface area, liquid waste volume and total tank volume. Also, solution as an initial value problem requires initial values for x and y.

If one assumes the mass transfer coefficient (k), ventilation rate (Q), volume of liquid waste in the tank (V_x) and generation rate remain constant (or nearly constant) and if m(x) varies linearly with x over the time period of interest, an analytical solution exists for Equations 1 and 2. This solution produces:

$$y=C_1e^{r_1t}+C_2e^{r_2t}+C_3, \qquad 3$$

where

$$r_{j=1,2}=\frac{-b\pm\sqrt{b^2-4ac}}{2a} \text{ and} \qquad 4$$

$$a = \frac{V_x V_y}{kAm}, \tag{5}$$

$$b = \left(\frac{V_x Q}{kAm} + \frac{V_x}{m} + V_y \right) \text{ and} \tag{6}$$

$$c = Q \text{, where} \tag{7}$$

$$C_3 = \frac{G}{Q}, \tag{8}$$

$$C_2 = -C_1 - C_3 + y_i \text{ and} \tag{9}$$

$$C_1 = \frac{\dfrac{x_i kAm}{V_y} + C_3 r_2}{r_1 - r_2} - y_i \frac{r_2 + \dfrac{Q}{V_y} + kA}{r_1 - r_2}. \tag{10}$$

For the liquid phase concentration, we get

$$x_i = \frac{\dfrac{V_y dy}{dt} + y_i Q}{kAm} + \frac{y_i}{m}, \tag{11}$$

$$\text{where } \frac{dy}{dt} = C_1 r_1 e^{r_1 t} + C_2 r_2 e^{r_2 t}. \tag{12}$$

However, lacking any of the conditions specified above (in particular a linear function m(x) or that the generation rate and ventilation rate remain constant over the time period of interest), no analytical solution exists for Equations 1 and 2. However, an approximate solution has been obtained using a numerical integration computer program.

Equations 3 and 11 indicate that the concentration of benzene in the liquid and vapor spaces depend on the mass transfer coefficient for benzene and a number of other measured or estimated parameters (see Appendix A). One can then provide estimates of the vapor and liquid benzene concentrations as a function of time for a given mass transfer coefficient. A measure of the validity of a given mass transfer coefficient derives from an error function for i measurements of the vapor or liquid space benzene concentration as:

$$SSE(k) = \sum_i \left(z_i - \hat{z}_i(k) \right)^2 \tag{13}$$

where z_i gives the measured concentration of benzene in the vapor or liquid space and $\hat{z}_i(k)$ denotes the predicted concentration of benzene in the vapor or liquid space. By evaluating this error function for various values of the mass transfer coefficient, one determines the value that minimizes this function as the best estimate mass transfer coefficient. The authors used separate methods to identify the best estimate of mass transfer coefficients for Tanks 50H and 48H as discussed in the following sections.

Best Estimate of Mass Transfer Coefficients

Tank 50H

From November 2, 1995 to January 31, 1996, ITP personnel made more than 80 individual measurements of either the liquid or vapor space benzene concentration in Tank 50H. During that period, the level in the tank ranged from 526,000 gallons to 748,000 gallons. The tank liquid and vapor temperature ranged from 27 to 31 °C and the number of pumps in operation ranged from 0 to 2. However, one may break this time period into 210 individual segments such that these variables – volume, temperature, and number of operating pumps -- remain constant over each segment.

The authors then solved for the benzene concentration in the vapor and liquid phase at the end of each time segment. With most of the required input parameters known (see Appendix A), the benzene generation rate remained the only unidentified value. Therefore, to provide an estimate of the mass transfer coefficient, the analysis must estimate the benzene generation rate simultaneously. Benzene production in Tank 50H during that time period likely came primarily from the decomposition of triphenylborane. (During this time period, a sufficient excess of potassium ion existed in Tank 50H to produce the precipitation of any tetraphenylborate ions present in the tank, thereby rendering these ions relatively unavailable for decomposition reaction.) The further assumption has been made that the decomposition of diphenylborinic acid and phenylborinic acid are relatively rapid upon their formation[5] and therefore the decomposition of a mole of triphenylborane effectively produces three moles of benzene. Note that from November 2 to November 9 of 1995, material was transferred from Tank 48H to Tank 50H. This material likely contained a significant quantity of triphenylborane. Since it was not possible to determine what quantity of triphenylborane was transferred to the tank during this time period, this analysis will assume that all of this triphenylborane was present on November 2. Thus, to provide an estimate of the benzene generation rate, one must estimate the initial triphenylborane concentration and the decomposition rate constant. Appendix A explains the method for converting this initial concentration into a benzene generation rate. Table A.1 gives the calculated benzene generation rate for the best estimate.

As indicated above, the analysis evaluated the error function not only for differing values of the mass transfer coefficient but also for the initial concentration of triphenylborane. Note that Table A.1 provides the number of pumps operated for each time segment. The mass transfer coefficient for 0 pumps does not depend on the mass transfer coefficient for either 1 or 2 pumps. Therefore, the analysis includes the mass transfer coefficient for 0 pumps as a variable for the error function. Therefore, the error function for Tank 50H is:

$$SSE(k_o,k_1,k_2,3PB_i,k_{3PB}) = \sum_i \left(z_i - \hat{z}_i(k_o,k_1,k_2,3PB_i,k_{3PB})\right)^2 \qquad 14$$

where k_0 is the mass transfer coefficient for 0 pumps, k_1 is the mass transfer coefficient for 1 pump, k_2 is the mass transfer coefficient for 2 pumps, $3PB_i$ is the initial concentration of triphenylborane and k_{3PB} is the decomposition rate constant for triphenylborane. Note that the mass transfer coefficient will change with tank level. The researchers assumed the mass transfer coefficient varies inversely proportionally to the fourth root of the tank volume, i.e.,[2]

$$k_1(V) = k_1(720,000)\left(\frac{720,000}{V}\right)^{\frac{1}{4}} \qquad 15$$

with k_1 (V) as the mass transfer coefficient for 1 pump at tank volume V (gallons) and k_1(720,000) as the mass transfer coefficient for 1 pump at tank volume 720,000 gallons. Table 1 contains the mass transfer coefficient employed for each of the steps evaluated for the best estimate case.

In determining the best estimate mass transfer coefficient, the authors adjusted all four parameters in Equation 14 simultaneously using the Microsoft© Excel Solver function.[3] Table 1 contains the optimized values for the three parameters. Table A.2 contains the measured values for Tank 50H and the input model evaluations for the best fit case.

Table 1. Best Estimate of Tank 50H Input Parameters.

Parameter	Value
k_{3PB} (hr^{-1})	0.0012
Triphenylborane (mg/L)	22
k_o (m/s)	2.6×10^{-7}
k_1 (m/s)	9.7×10^{-7}
k_2 (m/s)	1.5×10^{-6}

Note that the estimated decomposition rate constant falls within the range of measured decomposition rate constants for copper catalysis of triphenylborane decomposition.[5]

Mason, Gunst and Hess[4] indicate that any parameter set that produces an error function that falls within a certain range of the minimum error function does not significantly differ at a specified confidence interval. The following expression defines this range:

$$SSE = SSE_{\min}[1 + \frac{p}{n-p} F_\alpha(p, n-p)] \qquad 16$$

where p is the number of parameters (5), n is the number of data points (86), α is the confidence interval of interest (represented as a fraction) and the function F as the cumulative probability. For the system of interest, the 95% confidence interval becomes:

$$SSE = 1.14*SSE_{min} \qquad 17$$

Researchers used the Excel Solver function to determine the 95% cconfidence limits for k_0 between 2.0×10^{-7} and 3.5×10^{-7}, k_1 between 0.5×10^{-6} and 1.6×10^{-6} m/s and k_2 between 1.2×10^{-6} and 2.0×10^{-6} .Note that the confidence limits have been defined only for the mass transfer coefficients of interest and that the accuracy of the other input parameters has not been defined.

Tank 48H

On November 10, 1995, ITP operators started all four slurry pumps in Tank 48H and observed the release of benzene from the slurry to the vapor space. Table B.1 contains the data recorded from Tank 48H during that event. Note that over this time period, the temperature and ventilation rate varied. Therefore, Equations 1 and 2 require a numerical solution. This numerical solution uses a Runge-Kutta numerical integration subroutine. This work used one such subroutine (named SIVA and provided by Fortner Research). Appendix C contains a listing of the FORTRAN program "Data Regression" used to provide a numerical solution to Equations 1 and 2 based on the input data. The unshaded portions of Table B.1 comprise the input data file for the program. Appendix B also provides additional input information not contained in Table B.1.

In contrast to the evaluation for Tank 50H, the authors did not know the liquid phase benzene concentration in Tank 48H at the start of this operation. Also, the ~24 hour time period of interest involved continuous operation of 4 pumps. Also note that the generation of benzene during this time period likely came primarily from the decomposition of tetraphenylborate. During the time period of interest, the tetraphenylborate concentration likely remained nearly constant. However, as noted above, a significant rise in temperature occurred during this release event. Appendix B provides the temperature correction to the base benzene generation rate. Therefore, for this benzene release event, Equation 14 becomes:

$$SSE(k_4, x_i, Gen_{25}) = \sum_i \left(z_i - \hat{z}_i(k_4, x_i, Gen_{25})\right)^2 \qquad 18$$

where k_4 is the mass transfer coefficient for 4 pumps, x_i is the initial benzene concentration in the liquid phase and Gen_{25} is the benzene generation rate normalized to 25 °C. The program "Data Regression" evaluates the error function for given k_4, x_i and Gen_{25}. In addition, the program will search for the set of k_4, x_i and Gen_{25} values that minimizes the error function to provide the best estimate. Chart C.1 gives the methodology followed in this minimization. Table 2 contains the best estimate values for k_4, x_i and Gen_{25}.

Table 2. Best Estimate Tank 48H Input Parameters

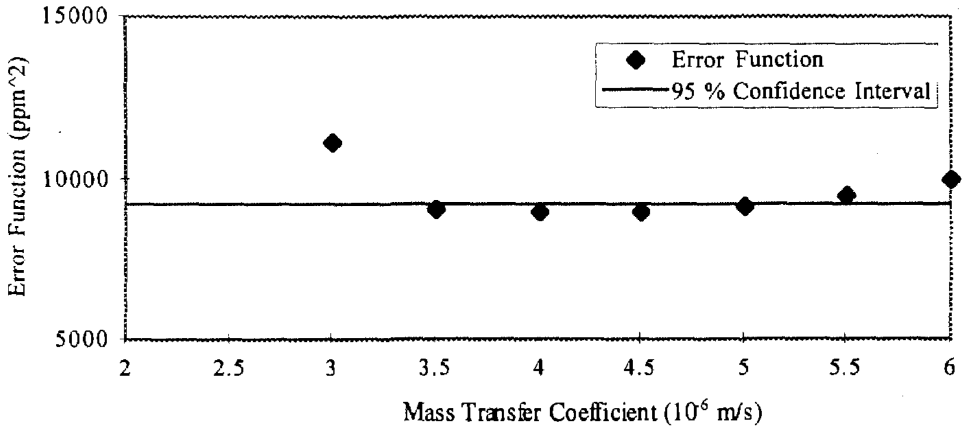
Parameter	Value
k_4 (m/s)	4.0×10^{-6}
x_i (mg/L)	123
Gen_{25} (μg/L/hr)	67.5

For this release event, Equation 17 becomes

$$SSE = 1.03 * SSE_{min} \qquad 19$$

Figure 1 contains a plot of the error function minimized for various values of k_4. Inspection of this Figure indicates upper and lower 95% confidence values for k_4 of 5.5×10^{-6} and 3.0×10^{-6}, respectively. Note that the confidence limits have been defined only for the mass transfer coefficient of interest and that the accuracy of the other input parameters has not been defined.

Figure 1. Error Function for Tank 48H as a Function of Mass Transfer Coefficient



CONCLUSIONS

Researchers developed methods for estimating mass transfer coefficients for Tanks 50H and 48H. For Tank 50H this method employed an analytical solution to the material balance equations governing mass transfer. This analytical solution estimated the liquid and vapor space benzene concentration as a function of time based on parameter values for the mass transfer coefficients for 0 and 1 pump and the initial triphenylborane concentration. The authors adjusted these input parameters to minimize the error between the estimated benzene concentrations and measured benzene concentrations to produce best estimate values for the input parameters. The analysis also determined the confidence limits for the 1 pump mass transfer coefficient. The authors calculated a best estimate mass transfer coefficients for 1 pump and 2 pumps at a tank level of 720,000 gallons as 9.7×10^{-7} m/s and 1.5×10^{-6} respectively. The authors also provided 95% confidence limits for k_0 between 2.0×10^{-7} and 3.5×10^{-7}, k_1 between 0.5×10^{-6} and 1.6×10^{-6} m/s and k_2 between 1.2×10^{-6} and 2.0×10^{-6}.

The authors used a similar approach for Tank 48H employing a numerical solution to the material balance equations and utilizing the parameters of 4-pump mass transfer coefficient, the initial liquid phase benzene concentration and the normalized benzene generation rate at 25 °C. The authors calculated a best estimate mass transfer coefficient for 4 pumps at a tank level of 167,000 gallons as 4.0×10^{-6} m/s with a 95% confidence interval ranges between 3.0×10^{-6} to 5.5×10^{-6} m/s.

APPROVALS

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Appendix A. Input Parameters for Tank 50H

Tank Volume and Surface Area:

The total tank volume and surface area derive from simple functions of tank dimensions with known values. Facility personnel periodically record the liquid waste volumes for each tank. The volume remained relatively constant during the time segments of interest.

Vapor-Liquid Equilibrium

In simple binary systems, Henry's Law or Raoult's Law governs the vapor-liquid equilibrium. This analysis uses such an approach for Tank 50H. The calculations assume a Henry's Law constant of 3.5 for Tank 50H.[7] Though the Henry's Law constant changes with temperature, the change over the range of operating temperatures remains small (less than 3 %).

Ventilation Rate

Facility personnel reported the average ventilation rate for Tank 50H during the operations of interest as approximately 150 scfm (where standard temperature is defined as 25 °C for this measurement).

Initial Liquid Phase Benzene Concentration

Facility personnel obtained periodic liquid samples from Tank 50H. The analysis will adjust mass transfer coefficients to obtain the best possible agreement with this data set and with the measured vapor space concentrations in Tank 50H. (see Appendix D)

Generation Rate

For Tank 50H, the calculations use a benzene generation rate which assumes that each mole of triphenylborane (3PB) reacts to form 3 moles of benzene with a first order rate constant (k_{3PB}) (at 25 °C) and an assumed activation energy (E) of 82 kJ/mole.[5] The following equation calculates the change in 3PB concentration:

$$x_{3PB\,i} = x_{3PB,i-1}e^{-k_{3PB}t}, \qquad \text{A.1}$$

$$\text{where } \mathrm{k}_{\mathrm{3PB,T}} = \mathrm{k}_{\mathrm{3PB,28C}}\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{R}}\left(\frac{1}{\mathrm{T}} - \frac{1}{25+273}\right)}. \qquad \text{A.2}$$

In these equations, $x_{3PB,i}$ and $x_{3PB,i-1}$ represent the concentration of 3PB in the liquid at the current and previous time step, respectively, T represents the absolute temperature for time step in K and R represents the ideal gas constant in the appropriate units. For cases where the concentration changes further by dilution (i.e., addition of material from sources other than Tank 48H resulting in an increase in volume for Tank 50H), the analysis multiplies the result from equation (A.1) by $V_{y,i-1}/V_{y,i}$. For cases when some 3PB is removed during transfer ($3PB_{transfer}$) to Saltstone, the analysis calculates the amount lost due to transfer as

$$3PB_{transfer} = \frac{\left(x_{3PB\,i} - x_{3PB\,i-1}\right)}{2} * \left(V_{x\,i-1} - V_{x,i}\right). \qquad \text{A.3}$$

The amount of 3PB lost due to decomposition results from subtracting the $3PB_{transfer}$ from the change in total amount of 3PB in the tank. The moles of benzene produced were calculated by multiplying the moles of 3PB lost by 3, since the maximum of 3 moles of benzene would be produced from 3PB decomposition.

Table A.1. Input Data For Tank 50H and Model Estimates

Interval StartTime	Interval Finish	Temp (°C)	# Pumps	Tank Level (gal)	y-model (ppm - vol)	x-model (mg/L)	Generation (μg/L/hr)	k (m/s)
	11/2/95 0:00	31	0	526852	0.0	0.12		2.6E-07
11/2/95 0:00	11/3/95 0:00	31	0	565526	1.5	1.24	45.6	2.6E-07
11/3/95 0:00	11/4/95 0:00	31	0	613401	3.5	2.21	39.8	2.6E-07
11/4/95 0:00	11/5/95 0:00	31	0	652300	5.4	3.04	35.4	2.6E-07
11/5/95 0:00	11/6/95 0:00	31	0	701671	7.0	3.77	31.1	2.6E-07
11/6/95 0:00	11/7/95 0:00	31	0	742814	8.4	4.40	27.8	2.6E-07
11/7/95 0:00	11/8/95 0:00	31	0	744310	9.6	4.96	26.2	2.6E-07
11/8/95 0:00	11/13/95 0:00	31	0	747302	14.2	7.21	22.2	2.6E-07
11/13/95 0:00	11/19/95 0:00	31	0	748050	17.8	8.89	16.3	2.6E-07
11/19/95 0:00	11/20/95 5:14	31	0	748050	18.3	9.13	13.3	2.6E-07
11/20/95 5:14	11/20/95 7:48	31	2	748050	39.6	9.08	12.8	1.5E-06
11/20/95 7:48	11/30/95 0:00	31	0	718876	20.2	10.04	10.1	2.6E-07
11/30/95 0:00	11/30/95 5:10	31	0	718876	20.3	10.05	7.4	2.6E-07
11/30/95 5:10	11/30/95 7:59	31	2	718876	45.0	9.97	7.3	1.5E-06
11/30/95 7:59	12/3/95 0:00	28	0	718876	20.1	9.91	5.0	2.6E-07
12/3/95 0:00	12/3/95 15:35	29	0	718876	19.9	9.90	5.2	2.6E-07
12/3/95 15:35	12/3/95 23:58	29	2	718876	74.6	9.65	5.1	1.5E-06
12/3/95 23:58	12/6/95 0:00	28	0	718876	19.7	9.59	4.4	2.6E-07
12/6/95 0:00	12/6/95 1:05	28	0	718876	19.6	9.58	4.2	2.6E-07
12/6/95 1:05	12/11/95 8:06	30	2	718876	79.3	6.62	4.6	1.5E-06
12/11/95 8:06	12/11/95 12:00	30	0	718876	57.6	6.62	4.0	2.6E-07
12/11/95 12:00	12/11/95 23:23	31	0	718876	27.0	6.62	4.3	2.6E-07
12/11/95 23:23	12/12/95 8:07	28	2	718876	56.8	6.45	3.1	1.5E-06
12/12/95 8:07	12/12/95 12:00	28	0	718876	42.4	6.45	3.0	2.6E-07
12/12/95 12:00	12/13/95 0:00	31	0	590960	23.2	6.44	4.6	2.6E-07
12/13/95 0:00	12/16/95 0:00	29	0	590960	12.9	6.32	3.1	2.6E-07
12/16/95 0:00	12/18/95 5:00	28	0	590960	12.5	6.21	2.5	2.6E-07
12/18/95 5:00	12/18/95 12:20	28	2	590960	41.9	6.03	2.3	1.6E-06
12/18/95 12:20	12/20/95 17:52	28	0	590960	12.2	5.91	2.2	2.6E-07
12/20/95 17:52	12/20/95 20:56	29	2	590960	26.1	5.84	2.4	1.6E-06
12/20/95 20:56	12/21/95 12:20	30	0	541588	15.8	5.81	2.7	2.6E-07
12/21/95 12:20	12/21/95 15:53	30	0	541588	14.8	5.80	2.5	2.6E-07
12/21/95 15:53	12/21/95 17:14	30	2	541588	20.9	5.76	2.5	1.6E-06
12/21/95 17:14	12/21/95 17:29	30	0	541588	20.7	5.76	2.5	2.6E-07
12/21/95 17:29	12/21/95 20:00	27	2	541588	30.4	5.70	1.8	1.6E-06
12/21/95 20:00	12/21/95 20:19	27	0	541588	29.9	5.69	1.8	2.6E-07
12/21/95 20:19	12/21/95 22:00	27	0	541588	27.6	5.69	1.8	2.6E-07
12/21/95 22:00	12/22/95 8:00	29	2	546077	50.7	5.44	2.2	1.6E-06
12/22/95 8:00	12/22/95 8:42	29	0	546077	48.5	5.44	2.2	2.6E-07
12/22/95 8:42	12/22/95 11:55	29	2	546077	52.9	5.36	2.2	1.6E-06
12/22/95 11:55	12/22/95 12:35	29	0	546077	50.7	5.35	2.2	2.6E-07

Table A.1. Input Data For Tank 50H and Model Estimates

Interval StartTime	Interval Finish	Temp (°C)	# Pumps	Tank Level (gal)	y-model (ppm - vol)	x-model (mg/L)	Generation (µg/L/hr)	k (m/s)
12/22/95 12:35	12/22/95 15:11	29	2	546077	53.8	5.29	2.2	1.6E-06
12/22/95 15:11	12/22/95 17:28	29	0	546077	46.4	5.29	2.2	2.6E-07
12/22/95 17:28	12/22/95 19:26	27	0	546077	41.4	5.28	1.7	2.6E-07
12/22/95 19:26	12/22/95 21:50	27	2	546077	45.7	5.22	1.7	1.6E-06
12/22/95 21:50	12/22/95 22:05	27	0	546077	45.0	5.22	1.7	2.6E-07
12/22/95 22:05	12/23/95 7:19	30	0	548321	26.5	5.21	2.3	2.6E-07
12/23/95 7:19	12/23/95 13:22	30	2	548321	41.4	5.07	2.3	1.6E-06
12/23/95 13:22	12/23/95 13:52	30	2	548321	42.2	5.06	2.3	1.6E-06
12/23/95 13:52	12/23/95 19:12	30	0	548321	30.9	5.05	2.3	2.6E-07
12/23/95 19:12	12/23/95 21:18	27	2	548321	36.3	5.00	1.6	1.6E-06
12/23/95 21:18	12/23/95 21:28	27	0	548321	35.9	5.00	1.6	2.6E-07
12/23/95 21:28	12/23/95 21:53	27	0	548321	35.1	5.00	1.6	2.6E-07
12/23/95 21:53	12/24/95 0:15	31	2	547573	39.4	4.94	2.5	1.6E-06
12/24/95 0:15	12/24/95 0:35	31	0	547573	38.6	4.94	2.5	2.6E-07
12/24/95 0:35	12/24/95 2:53	31	2	547573	42.6	4.89	2.5	1.6E-06
12/24/95 2:53	12/24/95 20:05	31	0	547573	17.9	4.87	2.4	2.6E-07
12/24/95 20:05	12/24/95 23:15	32	2	547573	27.7	4.80	2.6	1.6E-06
12/24/95 23:15	12/25/95 11:08	31	0	549817	16.6	4.78	2.3	2.6E-07
12/25/95 11:08	12/25/95 1:15	31	0	549817	25.1	4.80	2.3	2.6E-07
12/25/95 1:15	12/25/95 11:08	31	0	549817	16.6	4.78	2.3	2.6E-07
12/25/95 11:08	12/25/95 13:52	31	1	549817	20.9	4.75	2.3	1.0E-06
12/25/95 13:52	12/25/95 19:10	31	0	549817	16.9	4.74	2.3	2.6E-07
12/25/95 19:10	12/25/95 19:55	28	0	549817	16.7	4.74	1.6	2.6E-07
12/25/95 19:55	12/25/95 22:21	28	2	549817	24.3	4.69	1.6	1.6E-06
12/25/95 22:21	12/26/95 0:25	31	1	552061	26.1	4.66	2.2	1.0E-06
12/26/95 0:25	12/26/95 19:52	26	0	552061	12.8	4.61	1.3	2.6E-07
12/26/95 19:52	12/26/95 21:16	26	2	552061	17.7	4.58	1.3	1.6E-06
12/26/95 21:16	12/26/95 23:11	26	2	552061	23.4	4.54	1.3	1.6E-06
12/26/95 23:11	12/27/95 19:47	30	0	552061	11.6	4.51	1.9	2.6E-07
12/27/95 19:47	12/27/95 22:46	33	2	552061	21.2	4.45	2.5	1.6E-06
12/27/95 22:46	12/27/95 23:15	33	0	552061	20.8	4.45	2.5	2.6E-07
12/27/95 23:15	12/28/95 15:45	30	0	552061	12.1	4.42	1.8	2.6E-07
12/28/95 15:45	12/28/95 21:00	27	0	552061	11.1	4.41	1.3	2.6E-07
12/28/95 21:00	12/28/95 23:40	27	2	552061	19.7	4.36	1.3	1.6E-06
12/28/95 23:40	12/28/95 23:50	27	0	552061	19.5	4.36	1.3	2.6E-07
12/28/95 23:50	12/29/95 16:13	30	0	552061	11.4	4.33	1.7	2.6E-07
12/29/95 16:13	12/29/95 20:23	33	0	552061	10.6	4.32	2.3	2.6E-07
12/29/95 20:23	12/29/95 23:00	33	2	552061	19.1	4.28	2.3	1.6E-06
12/29/95 23:00	12/30/95 15:25	33	0	552061	11.4	4.26	2.2	2.6E-07
12/30/95 15:25	12/31/95 10:55	33	0	552061	9.2	4.23	2.1	2.6E-07
12/31/95 10:55	1/1/96 14:35	33	0	552061	8.6	4.20	2.0	2.6E-07

Table A.1. Input Data For Tank 50H and Model Estimates

Interval StartTime	Interval Finish	Temp (°C)	# Pumps	Tank Level (gal)	y-model (ppm - vol)	x-model (mg/L)	Generation (µg/L/hr)	k (m/s)
1/1/96 14:35	1/2/96 0:48	33	0	552061	8.6	4.18	1.9	2.6E-07
1/2/96 0:48	1/2/96 2:48	33	0	552061	8.6	4.18	1.8	2.6E-07
1/2/96 2:48	1/2/96 7:00	33	0	552061	8.5	4.17	1.8	2.6E-07
1/2/96 7:00	1/3/96 0:27	33	0	552061	8.5	4.15	1.8	2.6E-07
1/3/96 0:27	1/3/96 2:35	33	2	552061	15.6	4.11	1.7	1.6E-06
1/3/96 2:35	1/3/96 7:21	33	0	552061	13.2	4.10	1.7	2.6E-07
1/3/96 7:21	1/3/96 20:00	33	0	552061	10.1	4.08	1.7	2.6E-07
1/3/96 20:00	1/3/96 22:15	33	2	552061	17.1	4.04	1.6	1.6E-06
1/3/96 22:15	1/3/96 23:00	33	2	552061	19.1	4.02	1.6	1.6E-06
1/3/96 23:00	1/4/96 8:25	34	0	552061	13.2	4.01	1.8	2.6E-07
1/4/96 8:25	1/4/96 10:54	34	0	552061	12.3	4.01	1.7	2.6E-07
1/4/96 10:54	1/4/96 16:04	34	2	552061	25.5	3.92	1.7	1.6E-06
1/4/96 16:04	1/4/96 17:25	34	0	552061	23.7	3.91	1.7	2.6E-07
1/4/96 17:25	1/4/96 19:51	33	2	552061	28.4	3.87	1.5	1.6E-06
1/4/96 19:51	1/5/96 14:09	29	0	552809	12.5	3.83	1.0	2.6E-07
1/5/96 14:09	1/5/96 15:00	29	0	552809	12.2	3.83	1.0	2.6E-07
1/5/96 15:00	1/6/96 1:45	31	2	552809	32.4	3.65	1.2	1.6E-06
1/6/96 1:45	1/6/96 2:30	31	0	552809	30.9	3.65	1.1	2.6E-07
1/6/96 2:30	1/6/96 11:53	31	0	552809	18.3	3.63	1.1	2.6E-07
1/6/96 11:53	1/6/96 14:58	31	0	552809	15.8	3.63	1.1	2.6E-07
1/6/96 14:58	1/7/96 6:10	31	0	554305	9.7	3.60	1.1	2.6E-07
1/7/96 6:10	1/7/96 10:05	31	2	554305	19.5	3.54	1.1	1.6E-06
1/7/96 10:05	1/7/96 10:40	31	0	554305	18.9	3.53	1.1	2.6E-07
1/7/96 10:40	1/7/96 10:45	31	0	554305	18.8	3.53	1.1	2.6E-07
1/7/96 10:45	1/7/96 20:59	30	2	554305	32.8	3.37	0.9	1.6E-06
1/7/96 20:59	1/7/96 21:10	30	0	554305	32.4	3.37	0.9	2.6E-07
1/7/96 21:10	1/7/96 22:02	30	0	554305	30.7	3.37	0.9	2.6E-07
1/7/96 22:02	1/8/96 7:35	30	2	554305	36.4	3.23	0.9	1.6E-06
1/8/96 7:35	1/8/96 14:10	30	0	554305	23.9	3.22	0.9	2.6E-07
1/8/96 14:10	1/8/96 14:25	30	0	554305	23.5	3.22	0.9	2.6E-07
1/8/96 14:25	1/8/96 18:56	30	2	554305	28.6	3.15	0.9	1.6E-06
1/8/96 18:56	1/8/96 19:16	32	0	554305	27.8	3.15	1.1	2.6E-07
1/8/96 19:16	1/8/96 22:55	32	2	554305	30.8	3.10	1.1	1.6E-06
1/8/96 22:55	1/8/96 23:35	32	0	554305	29.5	3.10	1.1	2.6E-07
1/8/96 23:35	1/9/96 14:11	31	2	556549	35.2	2.90	1.0	1.6E-06
1/9/96 14:11	1/9/96 14:26	31	2	556549	35.2	2.90	0.9	1.6E-06
1/9/96 14:26	1/9/96 15:15	31	0	556549	33.3	2.90	0.9	2.6E-07
1/9/96 15:15	1/9/96 22:59	29	2	556549	34.5	2.80	0.8	1.6E-06
1/9/96 22:59	1/9/96 23:55	29	0	556549	32.4	2.79	0.7	2.6E-07
1/9/96 23:55	1/10/96 15:00	31	0	556549	13.2	2.78	0.9	2.6E-07
1/10/96 15:00	1/10/96 19:35	31	0	556549	10.8	2.77	0.9	2.6E-07

Table A.1. Input Data For Tank 50H and Model Estimates

Interval StartTime	Interval Finish	Temp (°C)	# Pumps	Tank Level (gal)	y-model (ppm - vol)	x-model (mg/L)	Generation (µg/L/hr)	k (m/s)
1/10/96 19:35	1/10/96 19:50	31	0	556549	10.7	2.77	0.9	2.6E-07
1/10/96 19:50	1/10/96 23:30	30	2	556549	17.0	2.72	0.8	1.6E-06
1/10/96 23:30	1/11/96 1:10	30	2	556549	19.2	2.70	0.8	1.6E-06
1/11/96 1:10	1/11/96 1:27	31	2	556549	19.5	2.70	0.9	1.6E-06
1/11/96 1:27	1/11/96 6:00	31	0	556549	15.1	2.69	0.9	2.6E-07
1/11/96 6:00	1/11/96 10:06	31	0	556549	12.3	2.69	0.9	2.6E-07
1/11/96 10:06	1/11/96 17:15	31	0	556549	9.2	2.68	0.8	2.6E-07
1/11/96 17:15	1/11/96 19:41	29	2	556549	13.7	2.65	0.7	1.6E-06
1/11/96 19:41	1/11/96 20:00	29	0	556549	13.5	2.65	0.7	2.6E-07
1/11/96 20:00	1/11/96 22:45	29	0	556549	11.8	2.64	0.7	2.6E-07
1/11/96 22:45	1/12/96 0:00	34	2	556549	13.8	2.63	1.1	1.6E-06
1/12/96 0:00	1/12/96 2:23	34	0	556549	12.3	2.63	1.1	2.6E-07
1/12/96 2:23	1/12/96 6:00	34	2	556549	17.7	2.59	1.1	1.6E-06
1/12/96 6:00	1/12/96 8:00	34	2	556549	19.9	2.56	1.1	1.6E-06
1/12/96 8:00	1/12/96 10:21	34	2	556549	22.1	2.54	1.1	1.6E-06
1/12/96 10:21	1/12/96 13:50	34	0	556549	17.9	2.53	1.1	2.6E-07
1/12/96 13:50	1/12/96 21:59	29	2	556549	24.7	2.44	0.6	1.6E-06
1/12/96 21:59	1/12/96 23:17	29	0	556549	22.7	2.44	0.6	2.6E-07
1/12/96 23:17	1/13/96 9:58	32	2	558045	26.7	2.33	0.9	1.6E-06
1/13/96 9:58	1/13/96 12:18	32	0	558045	22.8	2.32	0.8	2.6E-07
1/13/96 12:18	1/13/96 16:23	32	2	558045	24.6	2.28	0.8	1.6E-06
1/13/96 16:23	1/13/96 17:56	32	0	558045	22.2	2.28	0.8	2.6E-07
1/13/96 17:56	1/13/96 20:59	33	2	558045	23.5	2.25	0.9	1.6E-06
1/13/96 20:59	1/14/96 6:00	33	0	558045	13.6	2.24	0.9	2.6E-07
1/14/96 6:00	1/14/96 8:00	33	0	558045	12.2	2.24	0.9	2.6E-07
1/14/96 8:00	1/14/96 17:00	33	0	558045	8.2	2.23	0.9	2.6E-07
1/14/96 17:00	1/14/96 19:40	31	1	558045	10.2	2.22	0.7	1.0E-06
1/14/96 19:40	1/15/96 14:24	35	0	558045	5.6	2.20	1.0	2.6E-07
1/15/96 14:24	1/15/96 22:30	33	0	558045	5.1	2.20	0.8	2.6E-07
1/15/96 22:30	1/16/96 0:45	35	2	561038	8.9	2.17	1.0	1.6E-06
1/16/96 0:45	1/16/96 2:00	35	0	561038	8.5	2.17	0.9	2.6E-07
1/16/96 2:00	1/16/96 4:00	35	0	561038	7.9	2.17	0.9	2.6E-07
1/16/96 4:00	1/16/96 11:02	35	0	561038	6.4	2.17	0.9	2.6E-07
1/16/96 11:02	1/16/96 12:56	35	1	561038	8.0	2.16	0.9	1.0E-06
1/16/96 12:56	1/16/96 13:16	35	1	561038	8.2	2.15	0.9	1.0E-06
1/16/96 13:16	1/16/96 20:45	30	0	561038	6.5	2.15	0.5	2.6E-07
1/16/96 20:45	1/16/96 23:03	30	2	561038	10.1	2.12	0.5	1.6E-06
1/16/96 23:03	1/17/96 17:12	32	0	561038	5.5	2.10	0.6	2.6E-07
1/17/96 17:12	1/17/96 21:12	32	0	561038	5.2	2.10	0.6	2.6E-07
1/17/96 21:12	1/18/96 0:02	33	2	561038	9.6	2.07	0.7	1.6E-06
1/18/96 0:02	1/18/96 10:58	33	0	561038	6.4	2.06	0.7	2.6E-07

Table A.1. Input Data For Tank 50H and Model Estimates

Interval StartTime	Interval Finish	Temp (°C)	# Pumps	Tank Level (gal)	y-model (ppm - vol)	x-model (mg/L)	Generation (µg/L/hr)	k (m/s)
1/18/96 10:58	1/19/96 22:43	30	0	561038	4.3	2.02	0.5	2.6E-07
1/19/96 22:43	1/19/96 23:53	30	0	561038	4.2	2.02	0.4	2.6E-07
1/19/96 23:53	1/20/96 2:51	35	2	562534	8.8	2.00	0.7	1.6E-06
1/20/96 2:51	1/20/96 11:18	35	0	562534	6.4	1.99	0.7	2.6E-07
1/20/96 11:18	1/20/96 16:02	31	0	562534	5.7	1.98	0.5	2.6E-07
1/20/96 16:02	1/20/96 21:30	31	2	562534	12.6	1.94	0.5	1.6E-06
1/20/96 21:30	1/21/96 0:34	30	0	562534	10.7	1.93	0.4	2.6E-07
1/21/96 0:34	1/21/96 9:25	30	0	562534	7.1	1.92	0.4	2.6E-07
1/21/96 9:25	1/21/96 17:48	30	0	562534	5.5	1.91	0.4	2.6E-07
1/21/96 17:48	1/21/96 21:05	30	2	562534	9.9	1.88	0.4	1.6E-06
1/21/96 21:05	1/21/96 23:30	30	0	562534	8.8	1.88	0.4	2.6E-07
1/21/96 23:30	1/22/96 11:00	30	0	562534	5.7	1.87	0.4	2.6E-07
1/22/96 11:00	1/22/96 11:55	30	0	562534	5.6	1.87	0.4	2.6E-07
1/22/96 11:55	1/22/96 16:15	30	1	562534	8.3	1.85	0.4	1.0E-06
1/22/96 16:15	1/22/96 17:43	31	0	562534	7.8	1.84	0.4	2.6E-07
1/22/96 17:43	1/23/96 0:46	31	2	564778	14.4	1.79	0.4	1.6E-06
1/23/96 0:46	1/23/96 11:14	31	0	564778	8.1	1.78	0.4	2.6E-07
1/23/96 11:14	1/23/96 11:15	31	1	564778	8.1	1.78	0.4	1.0E-06
1/23/96 11:15	1/23/96 14:42	31	1	564778	9.6	1.76	0.4	1.0E-06
1/23/96 14:42	1/23/96 16:25	31	1	564778	10.2	1.75	0.4	1.0E-06
1/23/96 16:25	1/24/96 0:40	30	0	564778	6.9	1.74	0.4	2.6E-07
1/24/96 0:40	1/24/96 9:24	30	0	564778	5.1	1.73	0.3	2.6E-07
1/24/96 9:24	1/24/96 12:15	30	0	564778	4.8	1.73	0.3	2.6E-07
1/24/96 12:15	1/24/96 12:53	30	1	565526	5.3	1.73	0.3	1.0E-06
1/24/96 12:53	1/24/96 13:43	30	2	565526	6.4	1.72	0.3	1.6E-06
1/24/96 13:43	1/24/96 18:06	30	1	565526	8.6	1.70	0.3	1.0E-06
1/24/96 18:06	1/24/96 18:16	30	0	565526	8.5	1.70	0.3	2.6E-07
1/24/96 18:16	1/24/96 19:37	31	1	565526	9.0	1.69	0.4	1.0E-06
1/24/96 19:37	1/25/96 22:45	31	0	565526	4.0	1.67	0.4	2.6E-07
1/25/96 22:45	1/26/96 22:00	31	0	565526	3.4	1.65	0.3	2.6E-07
1/26/96 22:00	1/27/96 17:13	30	0	565526	3.3	1.63	0.3	2.6E-07
1/27/96 17:13	1/27/96 19:22	30	1	565526	4.9	1.62	0.3	1.0E-06
1/27/96 19:22	1/28/96 0:00	31	1	565526	7.4	1.60	0.3	1.0E-06
1/28/96 0:00	1/28/96 9:16	31	0	565526	5.2	1.59	0.3	2.6E-07
1/28/96 9:16	1/28/96 9:28	31	1	565526	5.3	1.59	0.3	1.0E-06
1/28/96 9:28	1/28/96 12:26	31	1	565526	6.9	1.57	0.3	1.0E-06
1/28/96 12:26	1/28/96 14:04	31	0	565526	6.4	1.57	0.3	2.6E-07
1/28/96 14:04	1/28/96 21:29	31	0	565526	4.9	1.57	0.3	2.6E-07
1/28/96 21:29	1/29/96 16:51	30	0	565526	3.5	1.55	0.3	2.6E-07
1/29/96 16:51	1/29/96 21:57	30	0	565526	3.4	1.54	0.3	2.6E-07
1/29/96 21:57	1/30/96 11:30	30	0	565526	3.2	1.53	0.3	2.6E-07

Table A.1. Input Data For Tank 50H and Model Estimates

Interval StartTime	Interval Finish	Temp (°C)	# Pumps	Tank Level (gal)	y-model (ppm - vol)	x-model (mg/L)	Generation (µg/L/hr)	k (m/s)
1/30/96 11:30	1/30/96 17:52	30	0	565526	3.1	1.53	0.2	2.6E-07
1/30/96 17:52	1/30/96 17:53	30	0	565526	3.1	1.53	0.2	2.6E-07
1/30/96 17:53	1/30/96 22:00	30	1	566274	5.7	1.51	0.2	1.0E-06
1/30/96 22:00	1/31/96 12:09	30	0	567770	3.9	1.49	0.2	2.6E-07
1/31/96 12:09	1/31/96 21:30	30	1	567770	8.1	1.46	0.2	1.0E-06

Table A.2. Measured and model x and y data.

Time	y-model ppm vol	x-model mg/L	y-measured ppm vol	x-measured mg/L
11/2/95 0:00	0.00	0.12		0.12
12/3/95 0:00	20.10	9.91		8
12/20/95 20:56	26.13	5.84		6
12/21/95 12:20	15.82	5.81	20	
12/21/95 20:19	29.92	5.69		5.9
12/22/95 17:28	46.44	5.29	44.8	
12/22/95 22:05	44.97	5.22		5.3
12/23/95 13:22	41.35	5.07	39.7	
12/23/95 21:28	35.93	5.00		5.8
12/25/95 1:15	27.74	4.80		5.3
12/25/95 11:08	16.57	4.78		5.1
12/25/95 19:10	16.93	4.74	17	
12/26/95 21:16	17.67	4.58		4.6
12/27/95 23:15	20.77	4.45	22.8	4.8
12/28/95 15:45	12.12	4.42	12.3	
12/28/95 23:50	19.50	4.36	24	5.2
12/29/95 16:13	11.44	4.33	11.2	
12/29/95 23:00	19.11	4.28	20.7	4.7
12/30/95 15:25	11.40	4.26	10.7	
12/31/95 10:55	9.20	4.23	8.9	
1/1/96 14:35	8.64	4.20	7.6	
1/2/96 2:48	8.57	4.18		4.9
1/2/96 7:00	8.55	4.17	8.4	
1/3/96 7:21	13.23	4.10	12.1	
1/3/96 23:00	19.12	4.02		4.4
1/4/96 8:25	13.21	4.01	10.3	
1/5/96 14:09	12.51	3.83	10.2	3.6
1/6/96 2:30	30.90	3.65	35.7	3.3
1/6/96 11:53	18.26	3.63	16.8	
1/6/96 14:58	15.82	3.63	12.9	
1/7/96 10:05	19.47	3.54		3.1
1/7/96 10:40	18.89	3.53	19.8	
1/7/96 21:10	32.42	3.37	35.1	
1/8/96 14:10	23.90	3.22	22	
1/9/96 14:11	35.15	2.90	30.6	2.9
1/9/96 23:55	32.36	2.79	33.4	
1/10/96 15:00	13.25	2.78	12.5	
1/10/96 19:35	10.84	2.77	9.9	
1/10/96 23:30	17.00	2.72		3.5
1/11/96 1:10	19.19	2.70	22.1	
1/11/96 10:06	12.32	2.69	12.1	
1/11/96 19:41	13.73	2.65		1.2
1/11/96 20:00	13.51	2.65	14.2	

Table A.2. Measured and model x and y data.

Time	y-model ppm vol	x-model mg/L	y-measured ppm vol	x-measured mg/L
1/12/96 8:00	19.95	2.56		3
1/13/96 9:58	26.66	2.33		2.5
1/14/96 19:40	10.15	2.22		2.2
1/15/96 14:24	5.65	2.20	5.4	2.3
1/16/96 12:56	7.98	2.16	7.9	2
1/16/96 12:56	7.98	2.16	7.9	2
1/17/96 17:12	5.53	2.10	5.1	1.9
1/18/96 10:58	6.39	2.06	8.4	
1/19/96 22:43	4.26	2.02	5	2.1
1/20/96 2:51	8.77	2.00		1.7
1/20/96 11:18	6.41	1.99	6.3	
1/21/96 0:34	10.69	1.93	9.7	
1/21/96 9:25	7.15	1.92	6.3	
1/21/96 21:05	9.87	1.88		1.9
1/21/96 23:30	8.77	1.88	9.4	
1/22/96 11:00	5.70	1.87	5.2	
1/23/96 0:46	14.43	1.79	16.1	
1/23/96 11:15	8.14	1.78	6.5	
1/23/96 14:42	9.62	1.76	9.8	
1/24/96 0:40	6.90	1.74	6.3	
1/24/96 9:24	5.15	1.73	4.7	
1/24/96 13:43	6.36	1.72		1.7
1/24/96 19:37	8.99	1.69	9.9	
1/25/96 22:45	3.98	1.67	3.4	
1/26/96 22:00	3.44	1.65	2.9	
1/27/96 19:22	4.90	1.62	2.6	1.5
1/28/96 9:28	5.28	1.59	4.9	
1/28/96 14:04	6.41	1.57	6.6	
1/28/96 21:29	4.92	1.57	4.4	
1/30/96 11:30	3.19	1.53	2.8	
1/30/96 17:52	3.14	1.53	2	
1/30/96 22:00	5.73	1.51		1.7

Appendix B. Input Parameters for Tank 48H

Tank Volume and Surface Area:

The total tank volume and surface area come from simple functions of tank dimensions with known values. Table B.1 lists the liquid waste volume.[6] Note that in Table B.1, data points taken from facility measurements are indicated by boxes around the data while the remaining data was interpolated between each tank measurement.

Vapor-Liquid Equilibrium

Previously, researchers defined the vapor pressure over a salt solution containing benzene as:[7]

$$P_B = mX_B$$

where P_B denotes the partial pressure of benzene, m represents the Henry's Law constant and X_B gives the mole fraction of benzene in solution. In dilute solution, m defines the Henry's Law constant as:

$$m = \frac{C_{vap-sat}}{C_{liq-sat}} = \frac{P^o M_B}{RT}\left(\frac{1}{S_B}\right)$$

with P^o as the vapor pressure of benzene (atm), M_B as the molecular weight of benzene (78 g/mole), R as the ideal gas constant (0.082055 L*atm/(mole*K) and S_B as the solubility of benzene in g/L.

Researchers also previously measured the solubility of benzene and found the following equations valid:[7]

$$S_B = 1.7689e^{-0.4481[Na^+]} \text{ at } 23\ ^\circ\text{C}$$

$$S_B = 1.9434e^{-0.4446[Na^+]} \text{ at } 40\ ^\circ\text{C}$$

$$S_B = 1.9811e^{-0.4075[Na^+]} \text{ at } 50\ ^\circ\text{C}$$

with [Na+] as the sodium ion concentration in solution. The solubility at temperatures between 23 °C and 50 °C comes from linear interpolation. Note that for the time period of interest the sodium ion concentration in Tank 48H was assumed to be approximately 4.7 M.

The literature contains the vapor pressure of benzene at a number of temperatures.[8] The following equation estimates this data over the temperature range of 25 to 60 °C:

$$P^O = (86.6 + .135{*}TEMP^2 - 3.011{*}TEMP)/760$$

where TEMP gives the temperature in °C.

Ventilation Rate

Table B.1 gives the average ventilation rate for Tank 48H.

Generation Rate

As temperature increase, the benzene generation rate will increase. The activation energy describes this increase in generation rate. For an activation energy of 50 kJ/mole, the generation rate for a given temperature (T) assume the form:

$$Gen(T) = Gen_{25} \frac{e^{\frac{-50{,}000}{R*(T+273)}}}{e^{\frac{-50{,}000}{R*298}}}$$

with T in °C.

Figure B.1 provides the best estimate fit to the tank vapor space measurements.

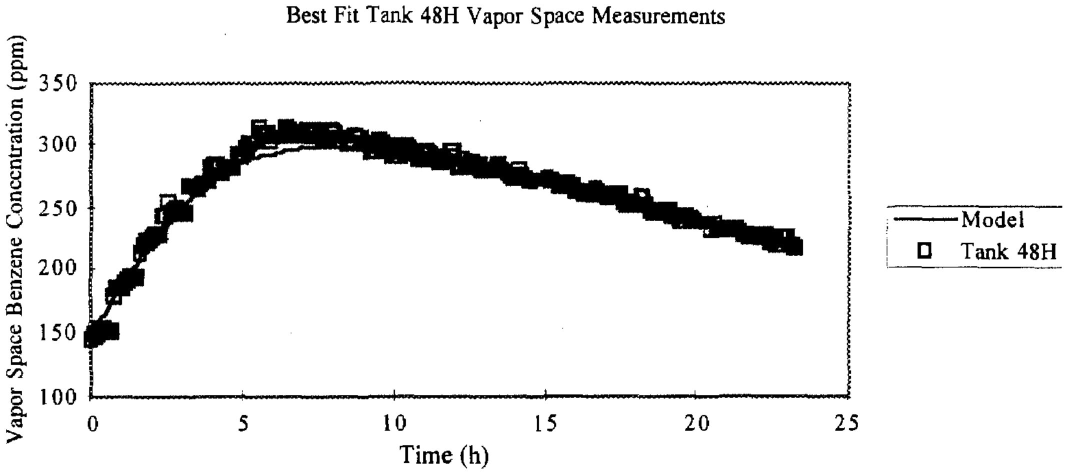


Table B.1. Input data file for Tank 48H

# of points	Tank level (gal)	Time step (min)
280	167000	5

Date	y-measured (ppm vol)	Q (scfm)	T Liq (°C)	T Vap (°C)	Pressure (in water)
10-Nov-95 9:45:04	145	780.857422	37.97	33.55	-0.5321211
10-Nov-95 9:49:58	148	779.064453	37.98	33.10	-0.5249492
10-Nov-95 9:55:00	147	777.218750	37.99	33.60	-0.5175664
10-Nov-95 10:00:03	149	775.390234	38.00	33.63	-0.5102188
10-Nov-95 10:04:57	152	775.350391	38.01	33.65	-0.5066328
10-Nov-95 10:09:59	152	775.309375	38.02	33.68	-0.5029414
10-Nov-95 10:15:01	151	775.268359	38.03	33.70	-0.4992500
10-Nov-95 10:20:04	151	775.227344	38.04	33.73	-0.4955586
10-Nov-95 10:24:58	151	775.187500	38.05	33.75	-0.4919727
10-Nov-95 10:30:00	179	775.146484	38.06	33.78	-0.4882813
10-Nov-95 10:35:02	185	769.076172	38.07	33.81	-0.4927930
10-Nov-95 10:39:56	185	763.179297	38.08	33.83	-0.4971758
10-Nov-95 10:44:59	184	757.108984	38.09	33.86	-0.5016875
10-Nov-95 10:50:01	188	751.038672	38.10	33.89	-0.5061992
10-Nov-95 10:55:03	191	744.968359	38.11	33.91	-0.5107109
10-Nov-95 10:59:57	193	739.071484	38.12	33.94	-0.5150937
10-Nov-95 11:05:00	193	736.616797	38.14	33.96	-0.5204180
10-Nov-95 11:10:02	193	734.196875	38.15	33.99	-0.5257500
10-Nov-95 11:15:04	193	731.776953	38.16	34.02	-0.5310820
10-Nov-95 11:19:58	212	729.426172	38.17	34.04	-0.5362617
10-Nov-95 11:25:00	219	727.006250	38.18	34.07	-0.5415937
10-Nov-95 11:30:03	222	724.583203	38.19	34.09	-0.5469648
10-Nov-95 11:34:57	221	721.913672	38.20	34.12	-0.5561289
10-Nov-95 11:39:59	223	719.165625	38.21	34.15	-0.5655625
10-Nov-95 11:45:01	226	716.417578	38.22	34.17	-0.5749961
10-Nov-95 11:50:04	227	713.669531	38.23	34.20	-0.5844297
10-Nov-95 11:54:58	227	711.000000	38.24	34.22	-0.5935937
10-Nov-95 12:00:00	227	708.251953	38.25	34.25	-0.6030273
10-Nov-95 12:05:02	243	708.539062	38.27	34.26	-0.6079492
10-Nov-95 12:09:56	244	708.817969	38.29	34.26	-0.6127305
10-Nov-95 12:14:59	253	709.105078	38.31	34.27	-0.6176523
10-Nov-95 12:20:01	246	709.392187	38.33	34.27	-0.6225742
10-Nov-95 12:25:03	247	709.679297	38.35	34.28	-0.6274961
10-Nov-95 12:29:57	249	709.958203	38.37	34.28	-0.6322773
10-Nov-95 12:35:00	246	707.401563	38.40	34.29	-0.6327305
10-Nov-95 12:40:02	246	704.817578	38.42	34.29	-0.6331406
10-Nov-95 12:45:04	246	702.233594	38.44	34.30	-0.6335508
10-Nov-95 12:49:58	246	699.723438	38.46	34.30	-0.6339492
10-Nov-95 12:55:00	265	697.139453	38.48	34.31	-0.6343594

Table B.1. Input data file for Tank 48H

Date	y-measured (ppm vol)	Q (scfm)	T Liq (°C)	T Vap (°C)	Pressure (in water)
10-Nov-95 13:00:03	268	694.542188	38.50	34.31	-0.6346953
10-Nov-95 13:04:57	267	690.677344	38.52	34.32	-0.6275234
10-Nov-95 13:09:59	265	686.698828	38.54	34.32	-0.6201406
10-Nov-95 13:15:01	264	682.720313	38.56	34.33	-0.6127578
10-Nov-95 13:20:04	267	678.741797	38.58	34.33	-0.6053750
10-Nov-95 13:24:58	270	674.876953	38.60	34.34	-0.5982031
10-Nov-95 13:30:00	270	670.898438	38.63	34.34	-0.5908203
10-Nov-95 13:35:02	270	674.753906	38.65	34.35	-0.5858984
10-Nov-95 13:39:56	281	678.499219	38.67	34.35	-0.5811172
10-Nov-95 13:44:59	283	682.354687	38.69	34.36	-0.5761953
10-Nov-95 13:50:01	284	686.210156	38.71	34.36	-0.5712734
10-Nov-95 13:55:03	281	690.065625	38.73	34.37	-0.5663516
10-Nov-95 13:59:57	276	693.810937	38.75	34.37	-0.5615703
10-Nov-95 14:05:00	278	690.069531	38.77	34.38	-0.5574609
10-Nov-95 14:10:02	282	686.255078	38.79	34.39	-0.5533594
10-Nov-95 14:15:04	282	682.440625	38.81	34.39	-0.5492578
10-Nov-95 14:19:58	282	678.735156	38.83	34.40	-0.5452734
10-Nov-95 14:25:00	282	674.920703	38.85	34.40	-0.5411719
10-Nov-95 14:30:03	291	671.269140	38.88	34.41	-0.5376836
10-Nov-95 14:34:57	289	684.178515	38.90	34.41	-0.5962539
10-Nov-95 14:39:59	289	697.467578	38.92	34.42	-0.6565469
10-Nov-95 14:45:01	291	710.756640	38.94	34.42	-0.7168398
10-Nov-95 14:50:04	296	724.045703	38.96	34.43	-0.7771328
10-Nov-95 14:54:58	300	736.955078	38.98	34.43	-0.8357031
10-Nov-95 15:00:00	302	750.244140	39.00	34.44	-0.8959961
10-Nov-95 15:05:02	302	748.808594	39.02	34.44	-0.8828711
10-Nov-95 15:09:56	302	747.414063	39.04	34.45	-0.8701211
10-Nov-95 15:14:59	313	745.978516	39.06	34.45	-0.8569961
10-Nov-95 15:20:01	310	744.542969	39.08	34.46	-0.8438711
10-Nov-95 15:25:03	308	743.107422	39.10	34.46	-0.8307461
10-Nov-95 15:29:57	309	741.712891	39.12	34.47	-0.8179961
10-Nov-95 15:35:00	301	736.946094	39.15	34.47	-0.8008086
10-Nov-95 15:40:02	305	732.147266	39.17	34.48	-0.7835820
10-Nov-95 15:45:04	305	727.348438	39.19	34.48	-0.7663555
10-Nov-95 15:49:58	305	722.686719	39.21	34.49	-0.7496211
10-Nov-95 15:55:00	305	717.887891	39.23	34.49	-0.7323945
10-Nov-95 16:00:03	305	713.145312	39.25	34.50	-0.7153359
10-Nov-95 16:04:57	312	714.221094	39.28	34.53	-0.7157344
10-Nov-95 16:09:59	314	715.328516	39.30	34.55	-0.7161445
10-Nov-95 16:15:01	311	716.435937	39.33	34.58	-0.7165547
10-Nov-95 16:20:04	310	717.543359	39.35	34.60	-0.7169648
10-Nov-95 16:24:58	307	718.619141	39.38	34.63	-0.7173633

Table B.1. Input data file for Tank 48H

Date	y-measured (ppm vol)	Q (scfm)	T Liq (°C)	T Vap (°C)	Pressure (in water)
10-Nov-95 16:30:00	305	719.726562	39.41	34.66	-0.7177734
10-Nov-95 16:35:02	306	720.669922	39.43	34.68	-0.7054688
10-Nov-95 16:39:56	306	721.586328	39.46	34.71	-0.6935156
10-Nov-95 16:44:59	306	722.529687	39.48	34.73	-0.6812109
10-Nov-95 16:50:01	312	723.473047	39.51	34.76	-0.6689063
10-Nov-95 16:55:03	312	724.416406	39.54	34.79	-0.6566016
10-Nov-95 16:59:57	310	725.332812	39.56	34.81	-0.6446484
10-Nov-95 17:05:00	311	728.266797	39.59	34.84	-0.6396563
10-Nov-95 17:10:02	305	731.219922	39.61	34.86	-0.6347344
10-Nov-95 17:15:04	305	734.173047	39.64	34.89	-0.6298125
10-Nov-95 17:19:58	303	737.041797	39.67	34.92	-0.6250313
10-Nov-95 17:25:00	303	739.994922	39.69	34.94	-0.6201094
10-Nov-95 17:30:03	303	742.945703	39.72	34.97	-0.6151758
10-Nov-95 17:34:57	303	745.575391	39.74	34.99	-0.6091992
10-Nov-95 17:39:59	311	748.282422	39.77	35.02	-0.6030469
10-Nov-95 17:45:01	310	750.989453	39.80	35.05	-0.5968945
10-Nov-95 17:50:04	306	753.696484	39.82	35.07	-0.5907422
10-Nov-95 17:54:58	306	756.326172	39.85	35.10	-0.5847656
10-Nov-95 18:00:00	306	759.033203	39.88	35.13	-0.5786133
10-Nov-95 18:05:02	306	759.402344	39.90	35.15	-0.5802539
10-Nov-95 18:09:56	299	759.760937	39.93	35.18	-0.5818477
10-Nov-95 18:14:59	299	760.130078	39.95	35.20	-0.5834883
10-Nov-95 18:20:01	299	760.499219	39.98	35.23	-0.5851289
10-Nov-95 18:25:03	308	760.868359	40.01	35.26	-0.5867695
10-Nov-95 18:29:57	305	761.226953	40.03	35.28	-0.5883633
10-Nov-95 18:35:00	305	764.114844	40.06	35.31	-0.5843164
10-Nov-95 18:40:02	301	767.026953	40.08	35.33	-0.5802148
10-Nov-95 18:45:04	301	769.939062	40.11	35.36	-0.5761133
10-Nov-95 18:49:58	299	772.767969	40.14	35.39	-0.5721289
10-Nov-95 18:55:00	294	775.680078	40.16	35.41	-0.5680273
10-Nov-95 19:00:03	294	778.551172	40.19	35.44	-0.5639805
10-Nov-95 19:04:57	294	777.196484	40.21	35.46	-0.5655742
10-Nov-95 19:09:59	294	775.801953	40.24	35.49	-0.5672148
10-Nov-95 19:15:01	304	774.407422	40.27	35.52	-0.5688555
10-Nov-95 19:20:04	302	773.012891	40.29	35.54	-0.5704961
10-Nov-95 19:24:58	298	771.658203	40.32	35.57	-0.5720898
10-Nov-95 19:30:00	296	770.263672	40.34	35.59	-0.5737305
10-Nov-95 19:35:02	297	770.796875	40.37	35.62	-0.5848047
10-Nov-95 19:39:56	290	771.314844	40.40	35.65	-0.5955625
10-Nov-95 19:44:59	290	771.848047	40.42	35.67	-0.6066367
10-Nov-95 19:50:01	290	772.381250	40.45	35.70	-0.6177109
10-Nov-95 19:55:03	290	772.914453	40.47	35.72	-0.6287852

Table B.1. Input data file for Tank 48H

Date	y-measured (ppm vol)	Q (scfm)	T Liq (°C)	T Vap (°C)	Pressure (in water)
10-Nov-95 19:59:57	296	773.432422	40.50	35.75	-0.6395430
10-Nov-95 20:05:00	298	775.875000	40.52	35.77	-0.6384297
10-Nov-95 20:10:02	297	778.335937	40.54	35.79	-0.6371992
10-Nov-95 20:15:04	295	780.796875	40.56	35.81	-0.6359688
10-Nov-95 20:19:58	294	783.187500	40.58	35.83	-0.6347734
10-Nov-95 20:25:00	292	785.648437	40.60	35.85	-0.6335430
10-Nov-95 20:30:03	287	787.861719	40.63	35.88	-0.6322422
10-Nov-95 20:34:57	287	764.991407	40.65	35.90	-0.6238750
10-Nov-95 20:39:59	287	741.448438	40.67	35.92	-0.6152617
10-Nov-95 20:45:01	294	717.905469	40.69	35.94	-0.6066484
10-Nov-95 20:50:04	293	694.362501	40.71	35.96	-0.5980352
10-Nov-95 20:54:58	291	671.492188	40.73	35.98	-0.5896680
10-Nov-95 21:00:00	287	647.949219	40.75	36.00	-0.5810547
10-Nov-95 21:05:02	289	663.371093	40.77	36.02	-0.5654688
10-Nov-95 21:09:56	288	678.352343	40.79	36.04	-0.5503281
10-Nov-95 21:14:59	285	693.774218	40.81	36.06	-0.5347422
10-Nov-95 21:20:01	285	709.196093	40.83	36.08	-0.5191563
10-Nov-95 21:25:03	285	724.617968	40.85	36.10	-0.5035703
10-Nov-95 21:29:57	285	739.599218	40.87	36.12	-0.4884297
10-Nov-95 21:35:00	294	742.021094	40.90	36.15	-0.4854375
10-Nov-95 21:40:02	294	744.317969	40.92	36.17	-0.4825664
10-Nov-95 21:45:04	289	746.614844	40.94	36.19	-0.4796953
10-Nov-95 21:49:58	282	748.846094	40.96	36.21	-0.4769063
10-Nov-95 21:55:00	283	751.142969	40.98	36.23	-0.4740352
10-Nov-95 22:00:03	287	753.401563	41.00	36.25	-0.4711328
10-Nov-95 22:04:57	281	751.728125	41.02	36.27	-0.4651563
10-Nov-95 22:09:59	281	750.005469	41.04	36.29	-0.4590039
10-Nov-95 22:15:01	281	748.282813	41.06	36.31	-0.4528516
10-Nov-95 22:20:04	286	746.560156	41.08	36.33	-0.4466992
10-Nov-95 22:24:58	284	744.886719	41.10	36.35	-0.4407227
10-Nov-95 22:30:00	282	743.164063	41.12	36.37	-0.4345703
10-Nov-95 22:35:02	283	743.902344	41.15	36.40	-0.4415430
10-Nov-95 22:39:56	280	744.619531	41.17	36.42	-0.4483164
10-Nov-95 22:44:59	277	745.357812	41.19	36.44	-0.4552891
10-Nov-95 22:50:01	278	746.096094	41.21	36.46	-0.4622617
10-Nov-95 22:55:03	278	746.834375	41.23	36.48	-0.4692344
10-Nov-95 22:59:57	278	747.551562	41.25	36.50	-0.4760078
10-Nov-95 23:05:00	278	746.339844	41.27	36.52	-0.4760742
10-Nov-95 23:10:02	283	745.109375	41.29	36.54	-0.4760742
10-Nov-95 23:15:04	282	743.878906	41.31	36.56	-0.4760742
10-Nov-95 23:19:58	280	742.683594	41.33	36.58	-0.4760742
10-Nov-95 23:25:00	278	741.453125	41.35	36.60	-0.4760742

Table B.1. Input data file for Tank 48H

Date	y-measured (ppm vol)	Q (scfm)	T Liq (°C)	T Vap (°C)	Pressure (in water)
10-Nov-95 23:30:03	276	740.227734	41.38	36.63	-0.4761523
10-Nov-95 23:34:57	273	739.550391	41.40	36.65	-0.4841211
10-Nov-95 23:39:59	272	738.853125	41.42	36.67	-0.4923242
10-Nov-95 23:45:01	272	738.155859	41.44	36.69	-0.5005273
10-Nov-95 23:50:04	272	737.458594	41.46	36.71	-0.5087305
10-Nov-95 23:54:58	279	736.781250	41.48	36.73	-0.5166992
11-Nov-95 0:00:00	275	736.083984	41.50	36.75	-0.5249023
11-Nov-95 0:05:02	273	735.878906	41.53	36.76	-0.5257227
11-Nov-95 0:09:56	271	735.679688	41.55	36.77	-0.5265195
11-Nov-95 0:14:59	270	735.474609	41.58	36.78	-0.5273398
11-Nov-95 0:20:01	272	735.269531	41.60	36.79	-0.5281602
11-Nov-95 0:25:03	271	735.064453	41.63	36.80	-0.5289805
11-Nov-95 0:29:57	271	734.865234	41.66	36.81	-0.5297773
11-Nov-95 0:35:00	271	737.544531	41.68	36.82	-0.5273477
11-Nov-95 0:40:02	271	740.251562	41.71	36.83	-0.5248867
11-Nov-95 0:45:04	271	742.958594	41.73	36.84	-0.5224258
11-Nov-95 0:49:58	274	745.588281	41.76	36.85	-0.5200352
11-Nov-95 0:55:00	270	748.295312	41.79	36.86	-0.5175742
11-Nov-95 1:00:03	271	750.975000	41.81	36.88	-0.5151055
11-Nov-95 1:04:57	269	750.815625	41.84	36.89	-0.5119180
11-Nov-95 1:09:59	267	750.651563	41.86	36.90	-0.5086367
11-Nov-95 1:15:01	265	750.487500	41.89	36.91	-0.5053555
11-Nov-95 1:20:04	265	750.323438	41.92	36.92	-0.5020742
11-Nov-95 1:24:58	265	750.164063	41.94	36.93	-0.4988867
11-Nov-95 1:30:00	269	750.000000	41.97	36.94	-0.4956055
11-Nov-95 1:35:02	267	748.154297	41.99	36.95	-0.4947852
11-Nov-95 1:39:56	266	746.361328	42.02	36.96	-0.4939883
11-Nov-95 1:44:59	261	744.515625	42.05	36.97	-0.4931680
11-Nov-95 1:50:01	262	742.669922	42.07	36.98	-0.4923477
11-Nov-95 1:55:03	262	740.824219	42.10	36.99	-0.4915273
11-Nov-95 1:59:57	259	739.031250	42.12	37.00	-0.4907305
11-Nov-95 2:05:00	259	738.769922	42.15	37.01	-0.4813789
11-Nov-95 2:10:02	259	738.523828	42.18	37.02	-0.4719453
11-Nov-95 2:15:04	259	738.277734	42.20	37.03	-0.4625117
11-Nov-95 2:19:58	262	738.038672	42.23	37.04	-0.4533477
11-Nov-95 2:25:00	263	737.792578	42.26	37.05	-0.4439141
11-Nov-95 2:30:03	262	737.594922	42.28	37.06	-0.4346211
11-Nov-95 2:34:57	259	742.296484	42.31	37.07	-0.4398008
11-Nov-95 2:39:59	259	747.136328	42.33	37.08	-0.4451328
11-Nov-95 2:45:01	257	751.976172	42.36	37.09	-0.4504648
11-Nov-95 2:50:04	258	756.816015	42.39	37.10	-0.4557969
11-Nov-95 2:54:58	258	761.517578	42.41	37.11	-0.4609766

Table B.1. Input data file for Tank 48H

Date	ymeasured (ppm vol)	Q (scfm)	T Liq (°C)	T Vap (°C)	Pressure (in water)
11-Nov-95 3:00:00	258	766.357422	42.44	37.13	-0.4663086
11-Nov-95 3:05:02	257	760.984375	42.46	37.14	-0.4663086
11-Nov-95 3:09:56	260	755.764844	42.49	37.15	-0.4663086
11-Nov-95 3:14:59	259	750.391797	42.52	37.16	-0.4663086
11-Nov-95 3:20:01	254	745.018750	42.54	37.17	-0.4663086
11-Nov-95 3:25:03	251	739.645703	42.57	37.18	-0.4663086
11-Nov-95 3:29:57	253	734.426172	42.59	37.19	-0.4663086
11-Nov-95 3:35:00	251	732.425000	42.62	37.20	-0.4740273
11-Nov-95 3:40:02	251	730.456250	42.65	37.21	-0.4818203
11-Nov-95 3:45:04	251	728.487500	42.67	37.22	-0.4896133
11-Nov-95 3:49:58	251	726.575000	42.70	37.23	-0.4971836
11-Nov-95 3:55:00	257	724.606250	42.72	37.24	-0.5049766
11-Nov-95 4:00:03	257	722.694531	42.75	37.25	-0.5127031
11-Nov-95 4:04:57	251	726.599219	42.77	37.27	-0.5135000
11-Nov-95 4:09:59	248	730.618750	42.78	37.29	-0.5143203
11-Nov-95 4:15:01	246	734.638281	42.80	37.31	-0.5151406
11-Nov-95 4:20:04	248	738.657812	42.81	37.33	-0.5159609
11-Nov-95 4:24:58	247	742.562500	42.83	37.35	-0.5167578
11-Nov-95 4:30:00	247	746.582031	42.84	37.38	-0.5175781
11-Nov-95 4:35:02	247	749.248047	42.86	37.40	-0.5155273
11-Nov-95 4:39:56	248	751.837891	42.87	37.42	-0.5135352
11-Nov-95 4:44:59	246	754.503906	42.89	37.44	-0.5114844
11-Nov-95 4:50:01	247	757.169922	42.91	37.46	-0.5094336
11-Nov-95 4:55:03	243	759.835937	42.92	37.48	-0.5073828
11-Nov-95 4:59:57	241	762.425781	42.94	37.50	-0.5053906
11-Nov-95 5:05:00	241	771.998046	42.95	37.52	-0.5013086
11-Nov-95 5:10:02	238	781.636718	42.97	37.54	-0.4972070
11-Nov-95 5:15:04	238	791.275390	42.98	37.56	-0.4931055
11-Nov-95 5:19:58	238	800.638671	43.00	37.58	-0.4891211
11-Nov-95 5:25:00	243	810.277343	43.02	37.60	-0.4850195
11-Nov-95 5:30:03	240	819.806250	43.03	37.63	-0.4809219
11-Nov-95 5:34:57	242	817.973438	43.05	37.65	-0.4773359
11-Nov-95 5:39:59	240	816.086719	43.06	37.67	-0.4736445
11-Nov-95 5:45:01	237	814.200000	43.08	37.69	-0.4699531
11-Nov-95 5:50:04	237	812.313281	43.09	37.71	-0.4662617
11-Nov-95 5:54:58	238	810.480469	43.11	37.73	-0.4626758
11-Nov-95 6:00:00	237	808.593750	43.13	37.75	-0.4589844
11-Nov-95 6:05:02	237	807.199219	43.14	37.77	-0.4708789
11-Nov-95 6:09:56	237	805.844531	43.16	37.79	-0.4824336
11-Nov-95 6:14:59	232	804.450000	43.17	37.81	-0.4943281
11-Nov-95 6:20:01	238	803.055469	43.19	37.83	-0.5062227
11-Nov-95 6:25:03	234	801.660938	43.20	37.85	-0.5181172

Table B.1. Input data file for Tank 48H

Date	y-measured (ppm vol)	Q (scfm)	T Liq (°C)	T Vap (°C)	Pressure (in water)
11-Nov-95 6:29:57	234	800.306250	43.22	37.87	-0.5296719
11-Nov-95 6:35:00	234	804.964844	43.23	37.90	-0.5480664
11-Nov-95 6:40:02	232	809.681640	43.25	37.92	-0.5665234
11-Nov-95 6:45:04	232	814.398437	43.27	37.94	-0.5849805
11-Nov-95 6:49:58	232	818.980469	43.28	37.96	-0.6029102
11-Nov-95 6:55:00	232	823.697265	43.30	37.98	-0.6213672
11-Nov-95 7:00:03	234	828.276172	43.31	38.00	-0.6396602
11-Nov-95 7:04:57	233	818.793360	43.33	38.02	-0.6408555
11-Nov-95 7:09:59	232	809.031641	43.34	38.04	-0.6420859
11-Nov-95 7:15:01	228	799.269922	43.36	38.06	-0.6433164
11-Nov-95 7:20:04	228	789.508204	43.38	38.08	-0.6445469
11-Nov-95 7:24:58	228	780.025391	43.39	38.10	-0.6457422
11-Nov-95 7:30:00	226	770.263672	43.41	38.13	-0.6469727
11-Nov-95 7:35:02	226	775.800781	43.42	38.15	-0.6490234
11-Nov-95 7:39:56	226	781.179687	43.44	38.17	-0.6510156
11-Nov-95 7:44:59	226	786.716797	43.45	38.19	-0.6530664
11-Nov-95 7:50:01	228	792.253906	43.47	38.21	-0.6551172
11-Nov-95 7:55:03	226	797.791015	43.48	38.23	-0.6571680
11-Nov-95 7:59:57	227	803.169922	43.50	38.25	-0.6591602
11-Nov-95 8:05:00	224	793.838282	43.53	38.26	-0.6595859
11-Nov-95 8:10:02	221	784.363672	43.55	38.27	-0.6599961
11-Nov-95 8:15:04	222	774.889063	43.58	38.28	-0.6604062
11-Nov-95 8:19:58	219	765.685157	43.60	38.29	-0.6608047
11-Nov-95 8:25:00	219	756.210547	43.63	38.30	-0.6612148
11-Nov-95 8:30:03	219	747.231248	43.66	38.31	-0.6616016
11-Nov-95 8:34:57	224	788.549217	43.68	38.32	-0.6596094
11-Nov-95 8:39:59	224	831.082420	43.71	38.33	-0.6575586
11-Nov-95 8:45:01	224	873.615623	43.73	38.34	-0.6555078
11-Nov-95 8:50:04	219	916.148826	43.76	38.35	-0.6534570
11-Nov-95 8:54:58	219	957.466795	43.79	38.36	-0.6514648
11-Nov-95 9:00:00	217	999.999998	43.81	38.37	-0.6494141

Appendix C. Fortran Code "Data Regression"

```
PROGRAM DATA REGRESSION
C
C
C    This program provides a regression of tank data to provide estimates of
C         mass transfer coefficients, initial benzene concentrations and benzene generation
rates
C    The program uses the SIVA subroutine to solve the differential material balance for the
C    tank vapor and liquid.  The SIVA subroutine is provided by Fortner Research
C    The program requires an input file containing time, temperature, vent rate and vapor
space
C    benzene concentration readings.  The program contains an input value for the tank
level.
C
C
C    This block initializes a number of variables for use in the program.
C
     PARAMETER (INEQ=3, IFDIM=16*INEQ+1, IYDIM=4*INEQ)
     INTEGER          NEQ, KORD(7), IOPT(9), TINT,NUMDATA
     REAL           TSPECS(4), T, H, DELT, TFINAL,AK1(6)
     REAL            F(IFDIM), Y(IYDIM),DATAIN (4,400),AFIT(7,30),EVALL(10,4)
          CHARACTER*40 LABEL,INNAME
    EXTERNAL SIVAO, SIVAF
     EQUIVALENCE (TSPECS(1), T), (TSPECS(2), H), (TSPECS(3), DELT),
    1  (TSPECS(4), TFINAL)
C
C    Common statements are used to pass a number of variables between subroutines
C
          COMMON / KPASS / AK1
          COMMON / ERR / ERROR
          COMMON / DATPASS / DATAIN
C
C    This block prints out a header prior to data input.
C
          WRITE (*,601)
          WRITE (*,602)

601       FORMAT (1X,'This program provides an estimate of Tank 48H benzene
concentration')
602       FORMAT (1X,'First, we need to input the data')

C
C    This block opens the data input file and reads in the data and writes the data
C    to the screen
C

     Open (unit=10,status='old',file='input.dat')
          Read (10,*) numdata,tankvol,delt
          WRITE (*,*) 'NUMBER OF DATA POINTS = ',NUMDATA

          do 57 ii = 1,numdata

          read (10,*) DATAIN(1,II),DATAIN(2,II),DATAIN(3,II),datain(4,ii)
```

```
          write (*,*) DATAIN(1,II),DATAIN(2,II),DATAIN(3,II),datain(4,ii)

57   CONTINUE
    CLOSE (UNIT = 10)
C
C    This block sets the tank volume in gallons: variable AK1(6)
C
          AK1(6) = tankvol
C
C  Input the initial mass transfer coefficient (m/s) (akio) and the step size (akstep)
C    of mass transfer coefficients to be investigated.
C

    write (*,607)
          read (*,*) akio,akstep

607   FORMAT (1X,'mass transfer coefficient plus step')


C
C         Sets the value for the F-tests
C
          EFTEST = (1+(3.0/(NUMDATA-3.0))*3.0)

C
C    The next block starts the evaluation loop for mass transfer coefficients.  The
C    first line sets the mass transfer cofficient - AKININ.  next, the initial concentration
C    is set - XIO, the initial step change in concentration, XISTEP and a holder for the
C    concentration, xii.
C
23   AKININ = AKIO + AKSTEP

          XISTEP = .1
          XIO = .001
          xii = 0.001

C
C    Nfist, nthird, nfour, nsecond, nfirst and nsecd are counters used to determine
C    location in the optimization routine.  x2 is the initial concentration.  gout and gi
C    are the initial generation rate, gstep is the initial step change in the generation
C    rate.
C

    nfist = 6
          nthird = 1
          nfour = 1
          x2 = 0.001

55   nsecond = 1
          gout = 0
          gi = 0
          gstep = 10
          nfirst = 1
          nsecd = 1
```

```
C
C    All generation rates are in 100 microg/l/min.  error is the error term for the
C     model fit (defined later). All concentration terms are in g/L passed
C
C          akin is the mass transfer coefficient.  ak1(1) is the mass transfer coefficient
C          times the area in units of l/min


191        agen = gout*1.66e-6
           error = 0

           XI=XII

           akin = akinin

           ak1(1) = 591*60*1000*akin

C
C    kall is a counter for the optimzation routine
C

           kall = 0
C
C    xgi and ak1(2) are the benzene generation rate in g/l/min
C
      XGI=agen
           ak1(2) = xgi
C
C    the next block sets the necessary input parameters to zero for the solver
C
      DO 502 I = 1,IYDIM
           Y(I) = 0
502   CONTINUE

      DO 503 I = 1,7
           KORD(I) = 0
503   CONTINUE

      DO 504 I = 1,9
           IOPT(I) = 0
504   CONTINUE
C
C    the next block sets the input parameters for the model.  The initial time is zero
C    the final time is for the last data point (in minutes).  The time step is the difference
C    between the first two data points (in minutes).  Note that the data points must be
C    evenly spaced.  Delt is the time step.  y(1) and xi is the initial liquid phase concentration
C    in mg/L.  y(2) is the gas phase concentration in ppm.
C
      T = 0
           TFINAL  = (datain(1,numdata)-datain(1,1))*24*60

c          DELT  = (DATAIN(1,2)-DATAIN(1,1))*24*60
           AK1(5) = DELT
```

```
c         WRITE (*,*) 'TFINAL =',TFINAL,delt,datain(1,2),datain(1,1)
          Y(1) = XI
          Y(2) = datain(2,1)
          Y(3) = 0

          F(1) = 0
          F(2) = 0
          F(3) = 0

C
C     The next block sets parameter requirements for the solution subroutine.
C
     NEQ=3
          H=100
          Y(4)=0.0E0
          Y(5)=0.0E0
     Y(3) = 0.0E0


C Set option for error control, local absolute error < 1.E-1.
      IOPT(1)=16
          IOPT(2)=7
          IOPT(3)=4

     KORD(7)=3
          F(4)=1.E-1
C Set option for second order equations
      IOPT(4) = 0

C
C Do the integration
C
     KORD(1) = 0
  100 CONTINUE
       CALL SIVA(TSPECS,Y,F,KORD,NEQ,SIVAF,SIVAO,4,IYDIM,IFDIM,7,IOPT)
       IF (KORD(1) .NE. 1) GO TO 100

C
C     these output lines can be used to print out output information to the screen
C     the first line prints out the generation rate and the error statement. the second
C     line prints out run control information
c
c         write (*,*) gout,error
c         write (*,*) nfirst,nsecond,nsecd,nfist
C
C     The following block starts the evaluation of the run control.
C

182       EVALL(nfirst,1) = error
          EVALL(nfirst,2) = gout


          if (nfirst .ge. 2) then
```

```
          gerr = abs((evall(nfirst,1)-evall(nfirst-1,1))/evall(nfirst,1))

         if (gerr .lt. .001) then
         goto 205
         endif

           if (evall(1,1) .lt. evall(2,1) ) then
     nsecd = 1
           nsecond = 1
           nfirst = 2
           evall(1,3) = evall(1,1)
           evall(1,4) = evall(1,2)
           gstep = (evall(2,2)-evall(1,2))/4
                gi = evall(1,2) + gstep
          gout = gi
           goto 191
          endif
         endif

    gout = gi + gstep
         gi = gi + gstep
         nfirst = nfirst + 1

         if (nfirst .ge. 6) then
         nsecond = 2
         endif

         if (nsecond .ge. 2) then
         goto 193
         endif

         goto 191

193   if (nsecd .ge. 2) then
    goto 183
         endif

168   kick = 0
         do 158 ijp = 1,3

         if (kick .le. 0) then
         if (evall(ijp+1,1) .lt. evall(ijp+2,1)) then
         nsecd = 2
         nsecond = 1
         nfirst = 4
         evall(1,3) = evall(ijp,1)
         evall(1,4) = evall(ijp,2)
         evall(3,3) = evall(ijp+1,1)
         evall(3,4) = evall(ijp+1,2)
         evall(5,3) = evall(ijp+2,1)
         evall(5,4) = evall(ijp+2,2)
         gi = (evall(ijp,2)+evall(ijp+1,2))/2
         gstep = ((evall(ijp+1,2)+evall(ijp+2,2))/2)-gi
```

```
          gout = gi
          kick = 1
          endif
          endif
158    continue

       if (kick .ge. 1) then
          goto 191
          endif

          if (gout .gt. 200) then
           WRITE (*,*) akin,xi,gout,error,nfist
          XII = XII + XISTEP
          XIO = XII
          IF (XII .GT. 2) THEN
          GOTO 305
          ELSE
          goto 55
          ENDIF
          endif

          nsecd = 1
          nsecond = 1
          nfirst = 3
          evall(1,1) = evall(4,1)
          evall(1,2) = evall(4,2)
          evall(2,1) = evall(5,1)
          evall(2,2) = evall(5,2)
          gi = evall(2,2) + gstep
          gout = gi
          goto 191



183    evall(2,3) = evall(4,1)
          evall(2,4) = evall(4,2)
          evall(4,3) = evall(5,1)
          evall(4,4) = evall(5,2)

          do 164 ijl = 1,5

          evall(ijl,1) = evall(ijl,3)
          evall(ijl,2) = evall(ijl,4)
164    continue
       goto 168


205    EVALL(nfist,1) = error
          EVALL(nfist,2) = xii
          write (*,*) akin,xi,gout,error,nfist
C         WRITE (*,*) 'INPUT NUMBER GREATER THAN 5 TO SEE OUTPUT'
          if (nfist .eq. 7) then
            if (evall(6,1) .lt. evall(7,1) ) then
```

```
       nfour = 1
            nthird = 1
            nfist = 7
            evall(6,3) = evall(6,1)
            evall(6,4) = evall(6,2)
            xistep = (evall(7,2)-evall(6,2))/4
            xio = evall(6,2) + xistep
                 xii = xio
            goto 55
           endif
          endif

      xii = xio + xistep
           xio = xio + xistep
           nfist = nfist + 1
             if (nfist .ge. 11) then
                  nthird = 2
                  endif
           if (nthird .ge. 2) then
           goto 141
           endif
           goto 55


 141    xerr = (evall(6,1)+evall(7,1)+evall(8,1)+evall(9,1)+evall(10,1))/5
     xss = 0

           do 115 iji = 1,5
           xss = (evall(iji+5,1)-xerr)**2 + xss
 115    continue

      xrat = (xss**.5)/xerr

           if (xrat .lt. .05) then
           goto 305
           endif

           IF (XII .GT. 2) THEN
           GOTO 305
           ENDIF

      if (nfour .ge. 2) then
      goto 133
           endif

 129   lkick = 0
           do 142 ijp = 1,3

           if (lkick .le. 0) then
           if (evall(ijp+6,1) .lt. evall(ijp+7,1)) then
           nfour = 2
           nthird = 1
           nfist = 9
           evall(6,3) = evall(ijp+5,1)
```

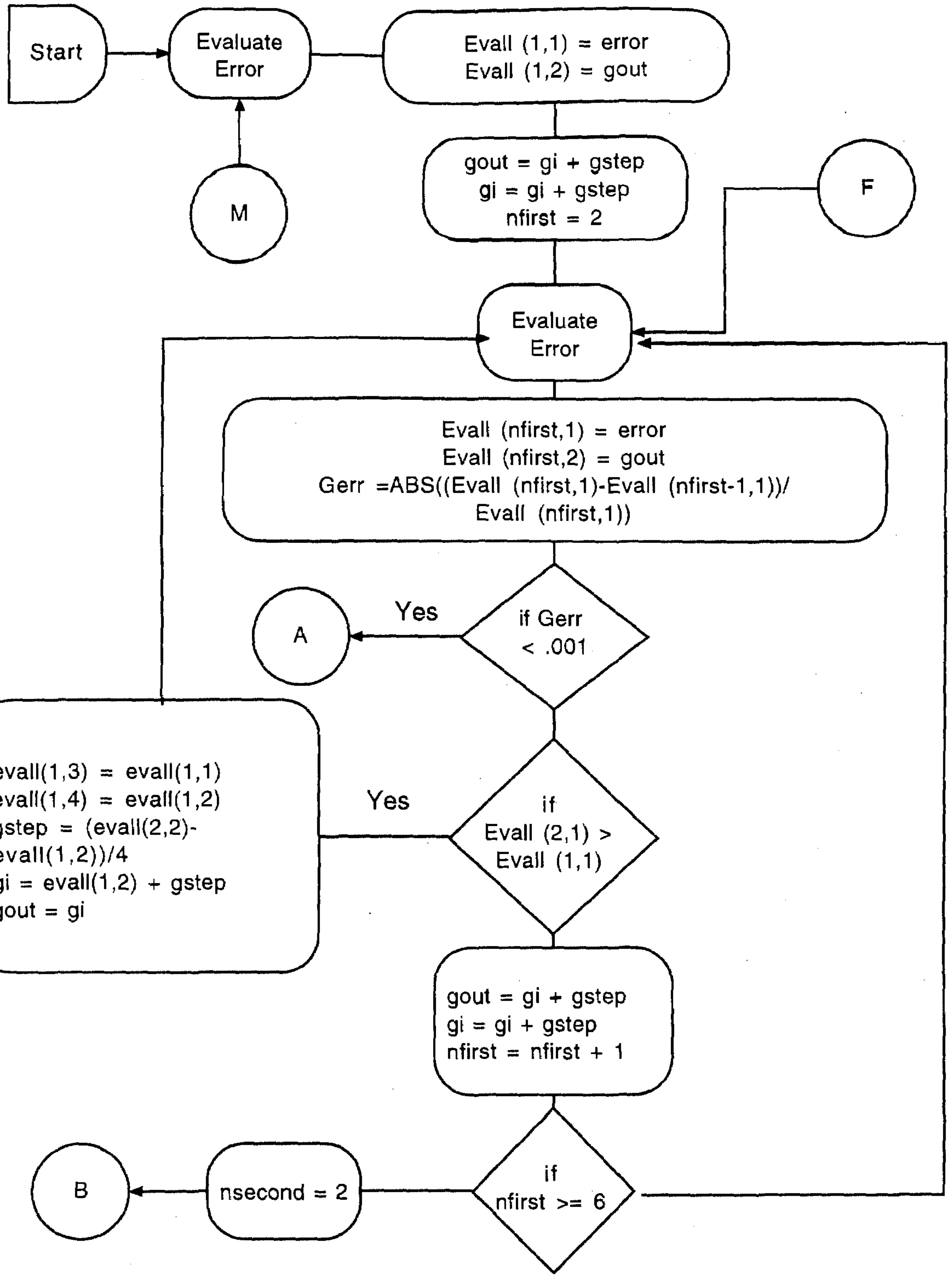
```
          evall(6,4) = evall(ijp+5,2)
          evall(8,3) = evall(ijp+6,1)
          evall(8,4) = evall(ijp+6,2)
          evall(10,3) = evall(ijp+7,1)
          evall(10,4) = evall(ijp+7,2)
          xio = (evall(ijp+5,2)+evall(ijp+6,2))/2
          xistep = ((evall(ijp+6,2)+evall(ijp+7,2))/2)-xio
          xii = xio
          lkick = 2
          endif
          endif
142   continue

      if (lkick .ge. 1) then
          goto 55
          endif

          if (xii .gt. 10) then
          goto 305
          endif

          nfour = 1
          nthird = 1
          nfist = 8
          evall(6,1) = evall(9,1)
          evall(6,2) = evall(9,2)
          evall(7,1) = evall(10,1)
          evall(7,2) = evall(10,2)
          xio = evall(7,2) + xistep
          xii = xio
          goto 55



133   evall(7,3) = evall(9,1)
          evall(7,4) = evall(9,2)
          evall(9,3) = evall(10,1)
          evall(9,4) = evall(10,2)

          do 166 ijl = 1,5

          evall(ijl+5,1) = evall(ijl+5,3)
          evall(ijl+5,2) = evall(ijl+5,4)
166   continue
      goto 129


305   write (*,*) 'for k = ',akio,xerr,xss
      akio = akinin
      if (akio .lt. 5e-5) then
          goto 23
          endif
```

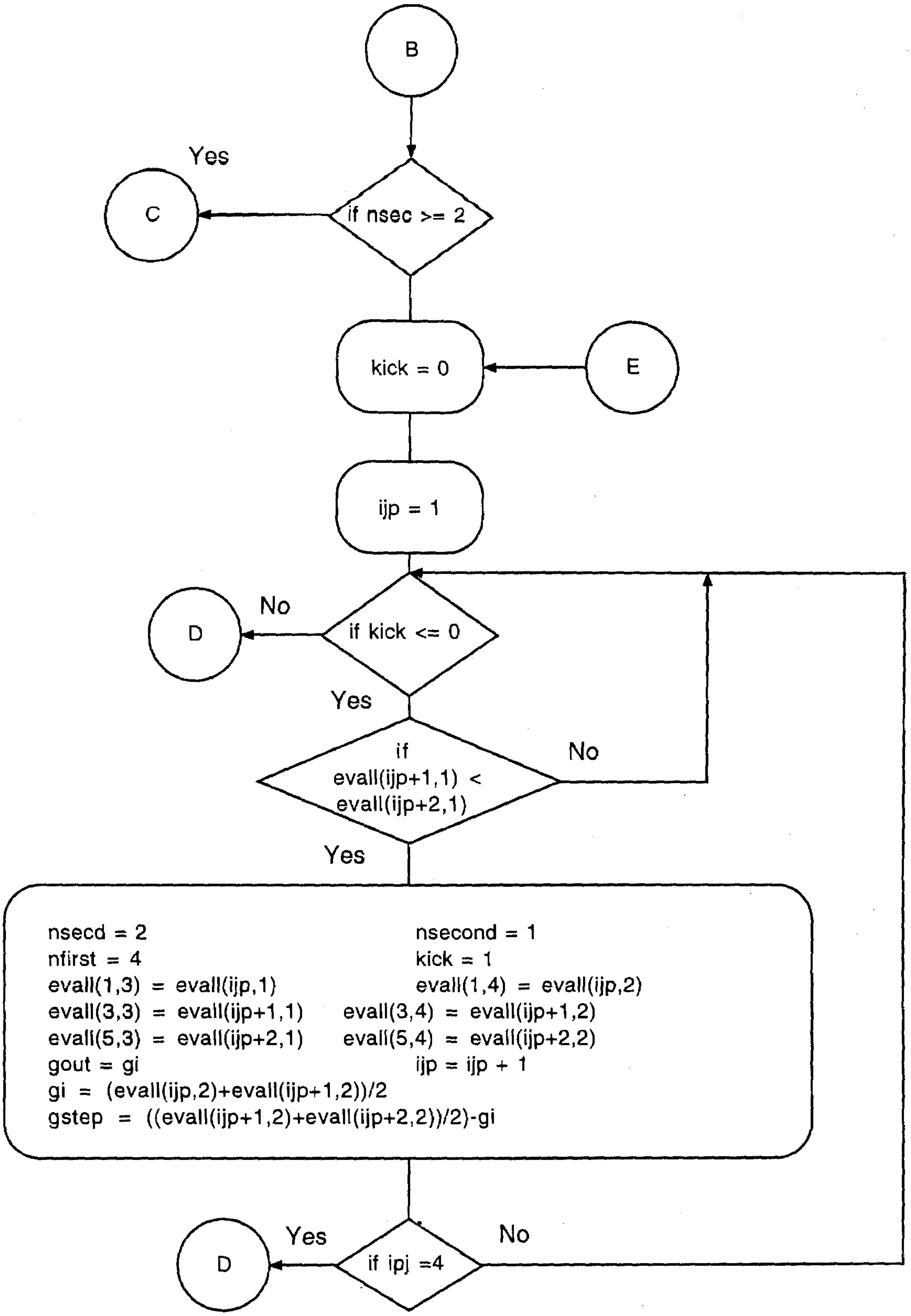
```
    STOP
    END

    SUBROUTINE SIVAF(T, Y, F, KORD)
C derivative subroutine for use with SIVA
C
    INTEGER        KORD,IITIME
    REAL           T, F(3), Y(6)
    REAL           TP
        REAL                     A,WK,WM,VY,G,VX,Q,AK1(6),DATAIN(4,400)
        INTRINSIC INT
        COMMON / KPASS / AK1
        COMMON / DATPASS / DATAIN
C
C       Evaluate the derivatives
C
C
C
C    Determine which time step the evaluation is in
C
        ttime = (t/(ak1(5))) + 1

        IITIME = INT(ttime)
C
C    determine the temperature during the time step
C
        TC = 273/(273+datain(4,iitime))
        TEMP = DATAIN(4,IITIME)
C
C evaluate the equilbrium vapor space benzene concentration: from DPST-88-661
C
    S23 = 1.789*exp(-.4481*4.7)
        S40 = 1.9434*exp(-.4446*4.7)
        S50 = 1.9811*exp(-.4075*4.7)

C
C    determine the solubility of benzenen in the slurry phase
C
        if (temp .gt. 40) then
              ssol = (((temp - 40)/10)*(s50-s40)) + s40
        else
          ssol = (((temp - 23)/17)*(s40-s23)) + s23
        endif
C
C    determine the equilibrium vapor space benzene concentration (in g/L)
C     correlation fit to bezene vapor pressure from Perry's Handbook.
    PO = (86.6 + .135*TEMP**2 - 3.011*TEMP)/760
        TK = temp + 273
        Ysol = 78*PO/(.082055*tk)

        if (y(1) .gt. ssol) then
        ystar = ysol
        else
        ystar = ysol*y(1)/ssol
```

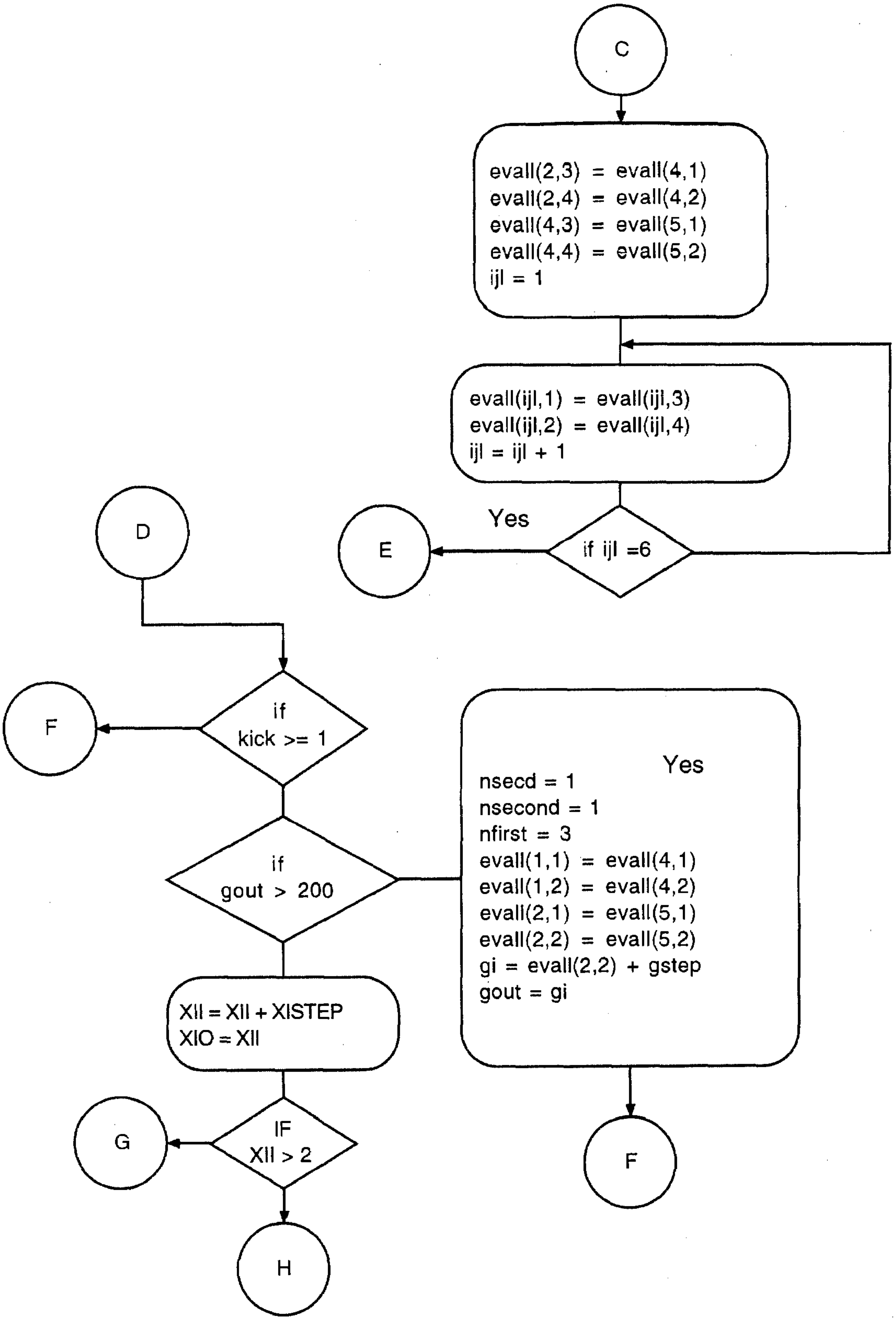
```
       endif

C
C   correct the vent rate (to scfm) for temperature
C
        VENTDAT = DATAIN(3,IITIME)*273/298
C
C   determine slurry volume in liters
c   and vapor space volume in 10e6 liters using standard conversions
c
       VOL = AK1(6)*3.788
       VVOL = (1.39e6-ak1(6))*3.788/1e6


C
C   correct the generation rate for temperature
C
C   Activation energy for decomposition. 5886 (K) = 50,000 kj/mole
     EA = 5886
     genr = ak1(2)*exp((EA/298)-(EA/TK))
C
C   evaluate the derivatives. note that y(3) is only a place holder.
C   3.479e-6 g/l/ppm
C   .28737 l/g for benzene vapor
C   28.3168 l/ft3
C


       F(1) = -AK1(1)*(YSTAR-3.479E-6*Y(2))/VOL + genr

    F(2) = ((0.28737*AK1(1)*(YSTAR-3.479E-6*Y(2))) - Y(2)*VENTDAT*28.3168E-
6)/(vvol*TC)

       F(3) =  2

       RETURN
     END

     SUBROUTINE SIVAO(TSPECS, Y, F, KORD)
      PARAMETER (INEQ=3, IFDIM=16*INEQ+1, IYDIM=4*INEQ)
      INTEGER       NEQ, KORD(7), IOPT(9), TINT,IIITIME
     REAL         TSPECS(4)
      REAL          F(IFDIM), Y(IYDIM),AK1(6),DATAIN(4,400),TTTIME
       INTRINSIC INT
       COMMON / ERR / ERROR
       COMMON / KPASS / AK1
       COMMON / DATPASS / DATAIN
C
C   this subroutine evaluates the fit to individual data points
C
C      determine the time step and the real time
C
     tttime = (TSPECS(1)/(ak1(5))) + 1
       IIITIME = INT(tttime)
```

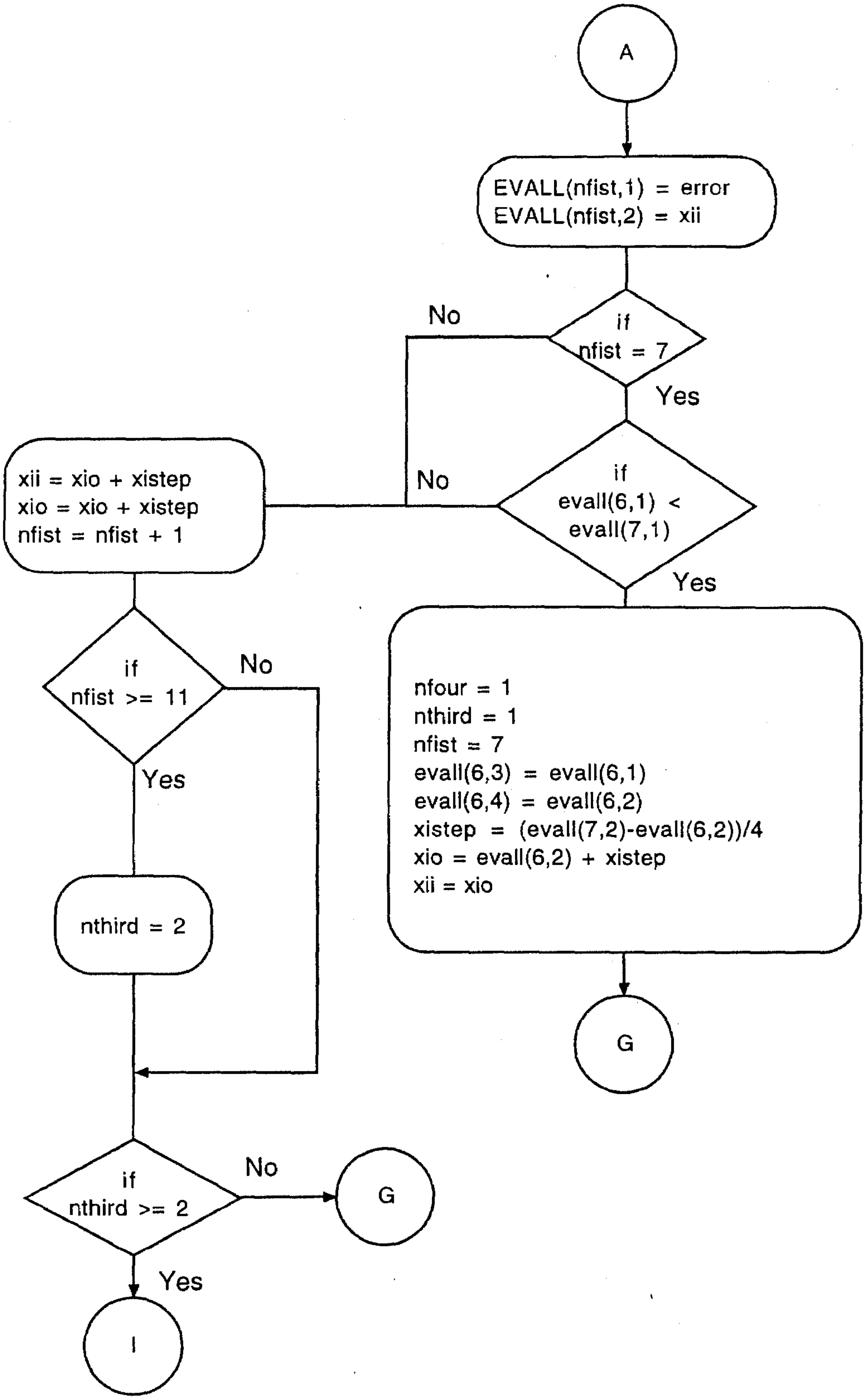
```
          ERROR = ERROR + (Y(2)-DATAIN(2,IIITIME))*(Y(2)-DATAIN(2,IIITIME))

      RETURN
      END
```

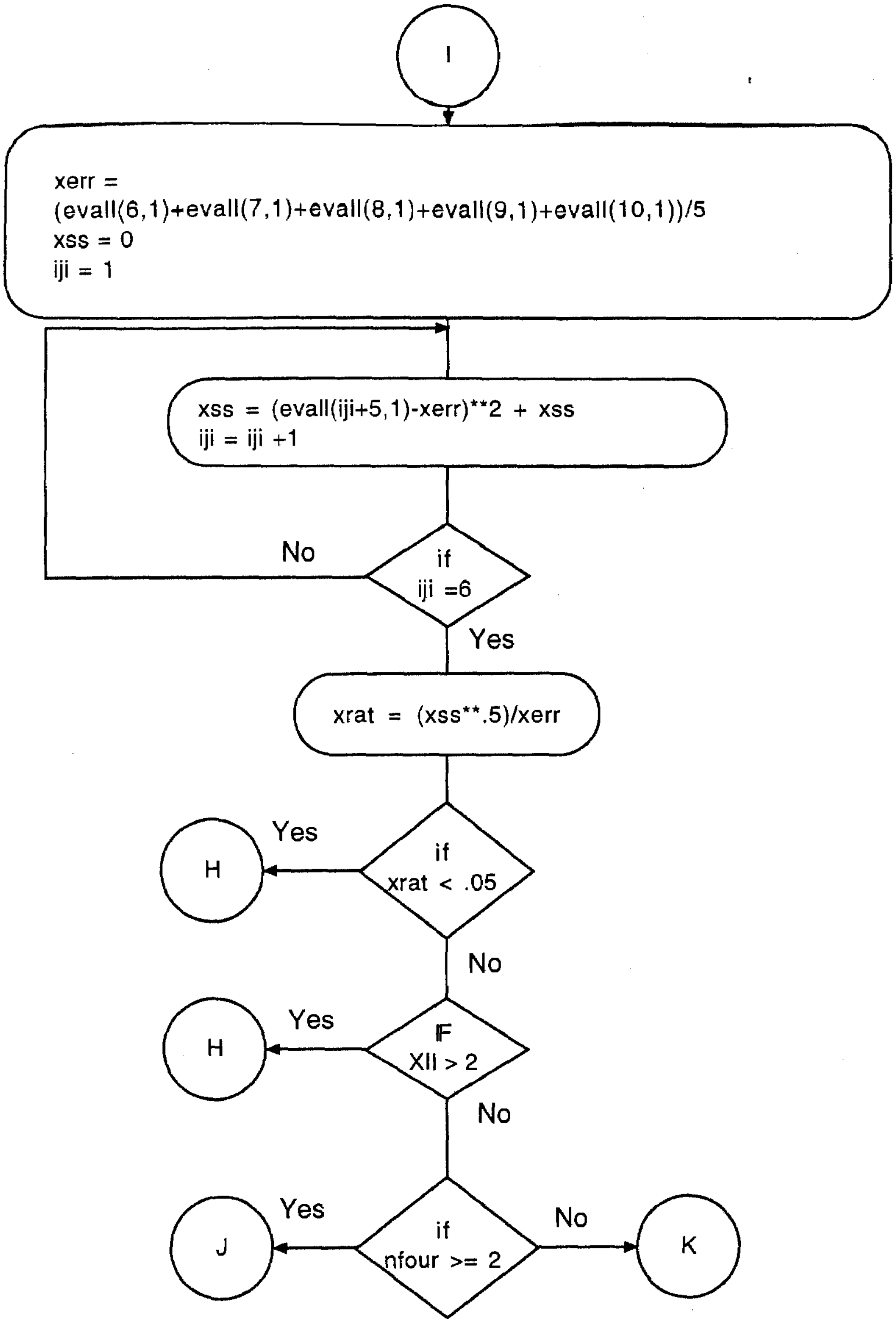
Figure C.1. Flowchart for optimization routine in program data regression.

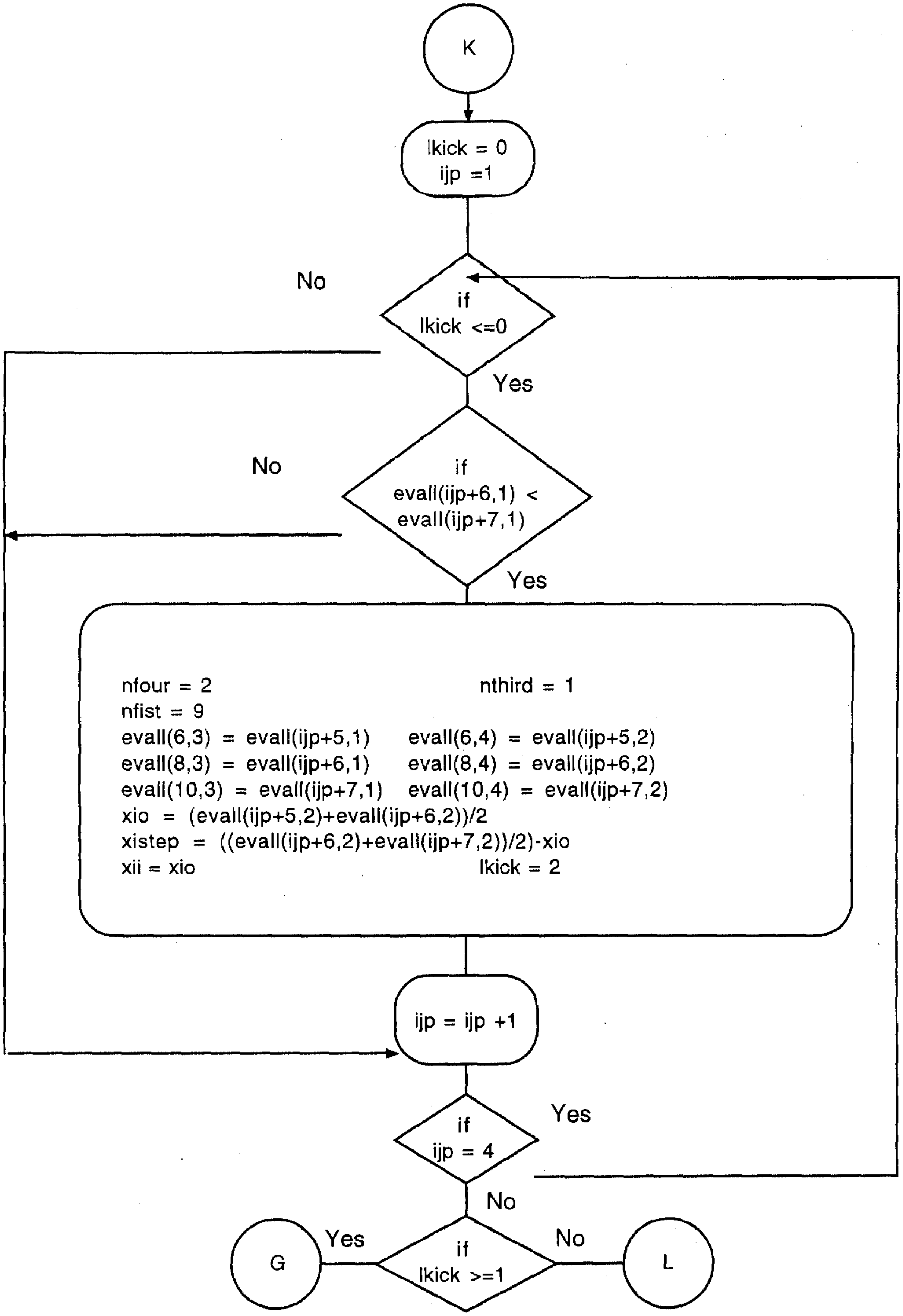


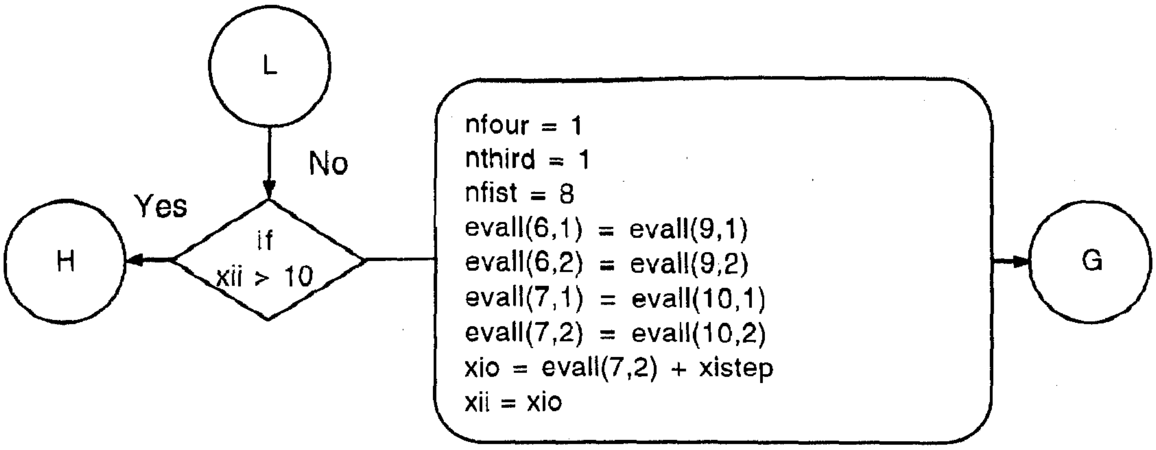

B
Yes
C
if nsec >= 2
kick = 0
E
ijp = 1
No
D
if kick <= 0
Yes
if
eval1(ijp+1,1) <
eval1(ijp+2,1)
No
Yes
nsecd = 2
nfirst = 4
evall(1,3) = evall(ijp,1)
evall(3,3) = evall(ijp+1,1)
evall(5,3) = evall(ijp+2,1)
gout = gi
gi = (evall(ijp,2)+evall(ijp+1,2))/2
gstep = ((evall(ijp+1,2)+evall(ijp+2,2))/2)-gi
nsecond = 1
kick = 1
evall(1,4) = evall(ijp,2)
evall(3,4) = evall(ijp+1,2)
evall(5,4) = evall(ijp+2,2)
ijp = ijp + 1
Yes
D
if ipj =4
No

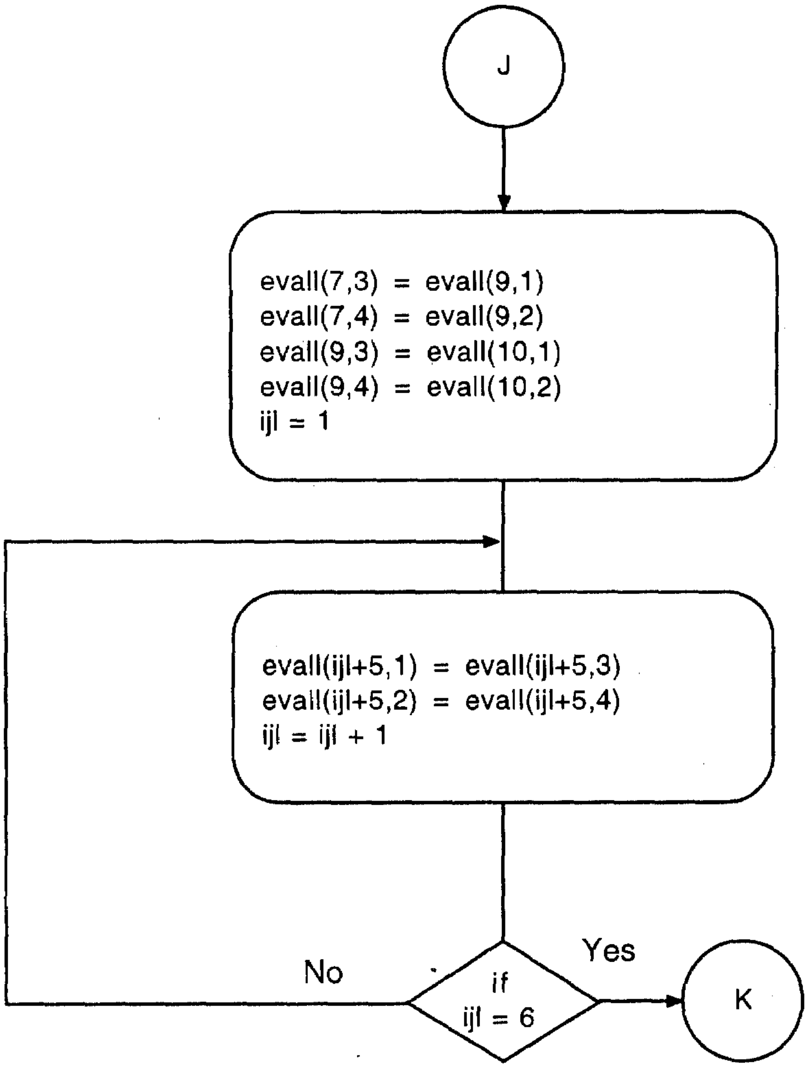

C
evall(2,3) = evall(4,1)
evall(2,4) = evall(4,2)
evall(4,3) = evall(5,1)
evall(4,4) = evall(5,2)
ijl = 1
evall(ijl,1) = evall(ijl,3)
evall(ijl,2) = evall(ijl,4)
ijl = ijl + 1
Yes
E
if ijl =6
D
F
if kick >= 1
Yes
nsecd = 1
nsecond = 1
nfirst = 3
evall(1,1) = evall(4,1)
evall(1,2) = evall(4,2)
evall(2,1) = evall(5,1)
evall(2,2) = evall(5,2)
gi = evall(2,2) + gstep
gout = gi
if gout > 200
XII = XII + XISTEP
XIO = XII
F
G
IF XII > 2
H

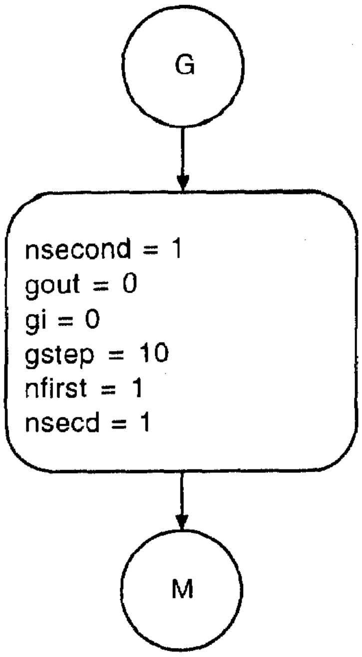

A
EVALL(nfist,1) = error
EVALL(nfist,2) = xii
if
nfist = 7
No
Yes
if
evall(6,1) <
evall(7,1)
No
Yes
xii = xio + xistep
xio = xio + xistep
nfist = nfist + 1
nfour = 1
nthird = 1
nfist = 7
evall(6,3) = evall(6,1)
evall(6,4) = evall(6,2)
xistep = (evall(7,2)-evall(6,2))/4
xio = evall(6,2) + xistep
xii = xio
G
if
nfist >= 11
No
Yes
nthird = 2
if
nthird >= 2
No
G
Yes
I

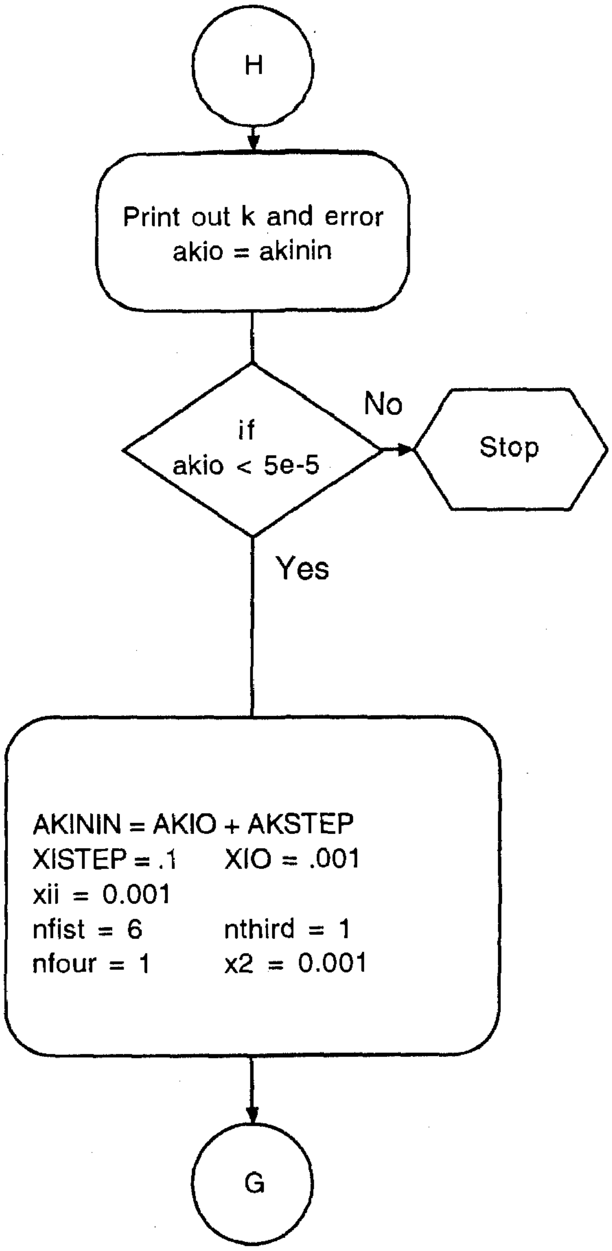

I
xerr =
(evall(6,1)+evall(7,1)+evall(8,1)+evall(9,1)+evall(10,1))/5
xss = 0
iji = 1
xss = (evall(iji+5,1)-xerr)**2 + xss
iji = iji +1
No
if
iji =6
Yes
xrat = (xss**.5)/xerr
Yes
H
if
xrat < .05
No
Yes
H
IF
XII > 2
No
Yes
J
if
nfour >= 2
No
K


K
lkick = 0
ijp =1
No
if
lkick <=0
Yes
No
if
evall(ijp+6,1) <
evall(ijp+7,1)
Yes
nfour = 2
nthird = 1
nfist = 9
evall(6,3) = evall(ijp+5,1)
evall(6,4) = evall(ijp+5,2)
evall(8,3) = evall(ijp+6,1)
evall(8,4) = evall(ijp+6,2)
evall(10,3) = evall(ijp+7,1)
evall(10,4) = evall(ijp+7,2)
xio = (evall(ijp+5,2)+evall(ijp+6,2))/2
xistep = ((evall(ijp+6,2)+evall(ijp+7,2))/2)-xio
xii = xio
lkick = 2
ijp = ijp +1
if
ijp = 4
Yes
No
G
Yes
if
lkick >=1
No
L


L
No
Yes
H
if
xii > 10
nfour = 1
nthird = 1
nfist = 8
evall(6,1) = evall(9,1)
evall(6,2) = evall(9,2)
evall(7,1) = evall(10,1)
evall(7,2) = evall(10,2)
xio = evall(7,2) + xistep
xii = xio
G


J
evall(7,3) = evall(9,1)
evall(7,4) = evall(9,2)
evall(9,3) = evall(10,1)
evall(9,4) = evall(10,2)
ijl = 1
evall(ijl+5,1) = evall(ijl+5,3)
evall(ijl+5,2) = evall(ijl+5,4)
ijl = ijl + 1
No
if
ijl = 6
Yes
K


G
nsecond = 1
gout = 0
gi = 0
gstep = 10
nfirst = 1
nsecd = 1
M


H
Print out k and error
akio = akinin
if
akio < 5e-5
No
Stop
Yes
AKININ = AKIO + AKSTEP
XISTEP = .1
XIO = .001
xii = 0.001
nfist = 6
nthird = 1
nfour = 1
x2 = 0.001
G

WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER

SRT-LWP-96-019

February 20, 1996

To: S. D. Fink, 773-A

From: R. F. Swingle, 773-A
C. J. Coleman, 773-A

Tank 50H Sample Results (U)

This document provides results of analyses of samples taken from Tank 50H during the period October 1995 - January 1996. Table 1 and Figures 1 and 2 give benzene analyses by the ITP lab of liquid and vapor samples taken from Tank 50H provided by W. C. Walker and R. M. Crouch of High Level Waste Engineering. Table 2 gives results of analyses performed by SRTC's Analytical Development Section on liquid samples taken from Tank 50H.

The results given in Table 1 are all from separate vapor and liquid samples taken at different times during the days noted on the table. The analyses were performed using gas chromatography. Temperature data for Tank 50H were taken twice each day, not necessarily at the time the samples were taken. The temperature data given in Figures 1 and 2 are for one of the daily temperature readings.

Benzene analyses in Table 2 were performed using gas chromatography-mass spec. Some of the Table 2 benzene analyses are suspect because the samples were placed in partially filled plastic containers and allowed to sit for several days before being analyzed. Tetraphenylborate analyses were performed using titration. All of the tetraphenylborate analyses were close to the lower limit of detection and should be considered suspect. Phenol and phenylboric acid (PBA) analyses were performed by high performance liquid chromatography. Analyses for PBA were requested after the original sample analyses, and the results indicated only very small amounts, below the lower limit of detection, present. Potassium analyses were performed by atomic absorbtion. Potassium analyses were also performed as requested after the original sample analyses and results are available for only two of the samples.

Table 1
Tank 50H Benzene Results from the ITP Lab

Date	Vapor (ppm)	Liquid (mg/L)
11/3/95		0.12
12/3/95		8.45
12/20/95		6.0
12/21/95	20.0	5.9
12/22/95	44.8	5.3
12/23/95	39.7	5.8
12/24/95	21.6	5.1
12/25/95	17.0	5.3
12/26/95	12.0	4.6
12/27/95	22.8	4.8
12/28/95	12.3	
12/28/95	24.0	5.2
12/29/95	11.2	
12/29/95	20.7	4.7
12/30/95	10.7	
12/31/95	8.9	
1/1/96	7.6	
1/2/96	8.4	4.9
1/3/96	12.1	4.4
1/4/96	10.3	
1/5/96	10.2	3.6
1/6/96	35.7	3.3
1/6/96	16.8	
1/6/96	12.9	
1/7/96	19.8	3.1
1/7/96	35.1	
1/8/96	22.0	
1/9/96	30.6	2.9
1/9/96	33.4	
1/10/96	12.5	
1/10/96	9.9	3.5
1/11/96	22.1	
1/11/96	12.1	
1/11/96	14.2	1.2
1/12/96		3.0
1/13/96		2.5
1/14/96		2.2
1/15/96	5.4	2.3
1/16/96	7.9	2.0
1/17/96	5.1	1.9
1/18/96	8.4	
1/19/96	5.0	2.1
1/20/96	6.3	1.7
1/21/96	9.7	
1/21/96	6.3	
1/21/96	9.4	1.9
1/22/96	5.2	
1/23/96	16.1	
1/23/96	6.5	
1/23/96	9.8	
1/24/96	6.3	
1/24/96	4.7	
1/24/96	9.9	1.7
1/25/96	3.4	
1/26/96	2.9	
1/27/96	2.6	1.5
1/28/96	4.9	
1/28/96	6.6	
1/28/96	4.4	
1/30/96	2.8	
1/30/96	2.0	1.7
1/31/96	5.8	
1/31/96	7.4	
2/4/96	2.3	
2/5/96	4.4	

Figure 1
Tank 50H Benzene Concentration for December

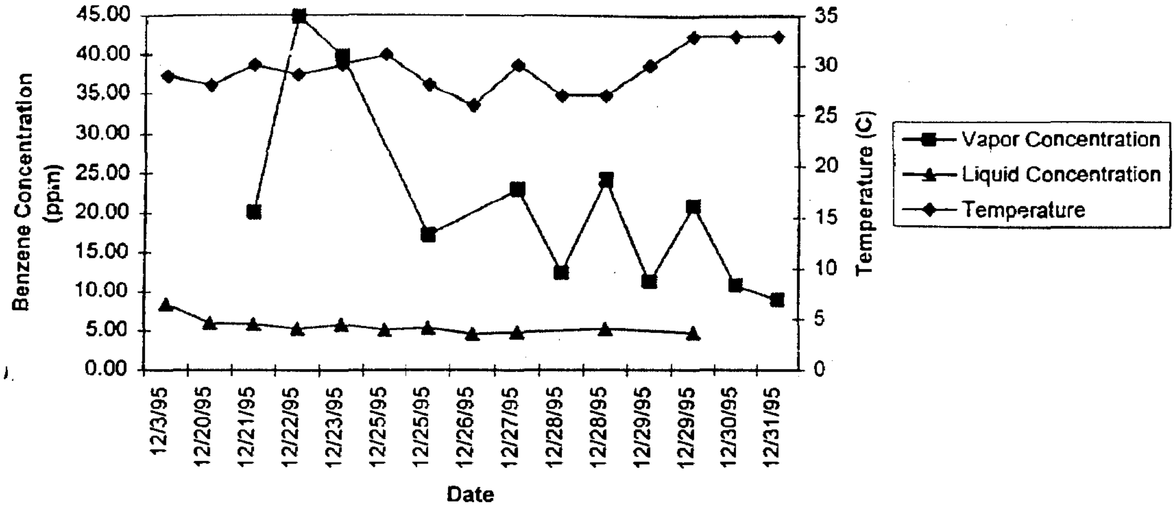
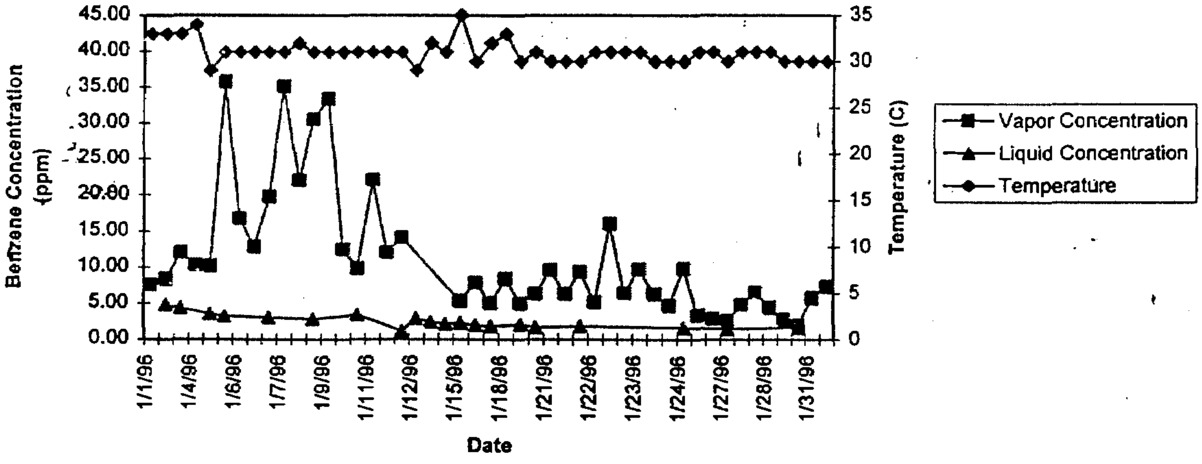


Figure 2
Tank 50H Benzene Concentration for January 1996



Note: Benzene concentration in Figures 1 and 2 is given in mg/L for liquid samples and ppm for vapor samples.

Table 2

SRTC-ADS Tank 50H Sample Analyses

Sample ID	Approx. Date	Benzene (mg/L)	Phenol (mg/L)	PBA (mg/L)	TPB (mg/L)	Total Potassium (mg/L)
ITP-155	10/4/95	<0.1 *	<0.15	na	542	na
ITP-193	11/5/95	0.12 *	98	<10	<628	na
ITP-209	12/3/95	8.5	120	<10	314	na
ITP-223	12/20/95	0.23 *	120	<10	<160	295
ITP-225	1/3/96	0.47 *	119	<10	<160	280
ITP-233	1/16/96	0.16	124	na	431	na

na - not available

* The starred benzene concentrations are suspected to be lower than the actual benzene concentration in Tank 50H at the time the sample was taken. The low results were probably caused by the samples being placed in partially filled.

cc:
J. F. Ortaldo, 704-S
R. M. Satterfield, 719-4A
L. M. Papouchado, 773-A
W. L. Tamosaitis, 773-A
D. D. Walker, 773-A
G. T. Wright, 703-H
L. A. Wooten, 730-2B
A. P. Christensen, 241-82B
G. D. Thaxton, 241-119H
J. R. Fowler, 704-Z
W. C. Walker, 241-82H
R. M. Crouch, 241-82H
J. E. Young, 773-A
C. W. Hsu, 773-A
H. D. Harmon, 719-4A
J. P. Morin, 719-4A
W. C. Clark, 240-119H
B. G. Croley, 240-120H
M. D. Johnson, 704-56H
C. A. Langton, 773-43A
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R. A. Peterson, 676-T
M. J. Barnes, 773-A
W. B. Van Pelt 676-1T
M. R. Poirier, 676-t
LWP Files

References

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[1] M.J. Montini and J.T. Carter, "Estimate Bounding MTCs for ITP Tanks and Provide Plans for Plant Tests", HLE-TTR-97019 (TL), June 18, 1997

[2] Y. Kawase and M. Moo-Young, "Mass Transfer at a Free Surface in Stirred Tank Bioreactors", Chemical Engineering Research and Design, March, 1990, V68 No. 2.

[3] R.F. Swingle, Laboratory Notebook, WSRC-NB-96-468, July 23, 1997.

[4] R.L. Mason, R.F. Gunst and J.L. Hess, "Statistical Design and Analysis of Experiments", John Wiley & Sons, 1989.

[5] C.L. Crawford and R.A. Peterson, "Decomposition Studies of Triphenylboron, Diphenylborinic Acid and Phenylboric Acid in Aqueous Alkaline Solutions Containing Copper (U)", WSRC-TR-97-0045, February 7, 1997.

[6] O. Cardona-Quiles, M.R. Williams, J.L. Kelly and D.A. Zupon, "Quick-Look Plots for SP-95-ITP-014 Slurry Pump Bump Test #3", HLW-ITP-950647, November 30, 1995.

[7] D.D. Walker, "Vapor Pressure of Benzene, Methanol, and Isopropanol Over Salt Solutions (U)", DPST-88-661, March 28, 1989.

[8] R.H. Perry and D. Green, "Perry's Chemical Engineers' Handbook", Sixth Edition, 1984, McGraw Hill.