APPENDIX B: INSTRUCTION FOR PERMEATION RATE WORKBOOK

1. ReadMe Spreadsheet

What this Workbook Is All About

This workbook enables the user to estimate the rate at which the weight of a permeation tube decreases. A linear relationship between the tube's weight and elapsed time is established. If the estimated weight at time zero is significantly different from the actual weight at time zero, then at least the earliest data pair should be removed from the analysis. Uncertainty of the slope estimate (the rate of weight loss or drift) will be determined. The traceability protocol requires that this estimate have a relative uncertainty of less than 1%.

How the Workbook Is Organized

The workbook consists of several worksheets, which are displayed as tabs on the bottom of the screen. Each worksheet performs a distinct function as described below.

ReadMe	describes the workbook and explains how to use the worksheets
Data	allows for user input of the calibration data (elapsed time and weight)
ANOVA	performs analysis of variance and determines whether the intercept term is needed
Calibration Results	calculates the drift and its uncertainty
Curve	graphically displays the drift line together with its confidence bands
Residual	graphically displays the vertical difference between the observed and estimated weights
Report	summarizes the assay results for a permeation device
Chart Data	includes the data used to create the curve and residual charts.

How the Worksheets Are Set up

Each worksheet contains instructions that guide the user through the steps in using the worksheet. The worksheets are also color-coded to simplify use. Shaded cells that are bordered in blue lines are cells whose contents you can change (i.e., enter data). In other sheets you can change the following variables:

Sheet	Variable	Location	Current Value
Data	Unit of Time	H22	m
Data	Unit of Weight	H24	g
Report	Device ID	F5	test data
Chart Data	significance level	D2	1.00E-05

Derived values are colored red. These cells contain formulas that should not be changed. The cells are protected to prevent alteration.

How to Use the Worksheets

Step 1: Enter the elapsed times (all in the same units) and corresponding tube weights in the Data worksheet. The worksheet will compute the total weight loss for each observation.

Step 2: Select the significance level (alpha) to be used in producing confidence limits for the estimated slope and intercept. Then review the results of the F-test and t-test to determine whether the intercept term is needed. If the intercept term is significant, then determine which of the early data points should be removed. Removing those data, and correcting the elapsed times, repeat Steps 1 and 2.

Step 3: Examine the corresponding Curve chart. You may need to adjust the chart's axis scaling. The points should appear to fall virtually on top of the black line. The black line should be very close to its confidence bands (colored red and blue).

Step 4: Examine the corresponding Residual worksheet. The residuals should appear to be random in both magnitude and direction. If they appear to follow a regular pattern, then the simple linear model is not appropriate. The device does not have a constant rate of weight loss. More time may be required to establish and measure a linear relationship. Observations taken before the linear relationship is established should be discarded and not used in the statistical analysis.

Step 5: Print the one-page report provided in the Report sheet. The report summarizes the assay data and indicates the uncertainty of the estimate.

2. Data Entry Worksheet

	Elapsed Time	Weight	Data Entry Worksheet
I	X_i	Y_i	Enter the data in the blue-bordered spaces. The first column (**X**) is for the elapsed time. The time of the first entry should be zero. The second column (**Y**) is for the tube weights.
0	0	4.354206	
1	8641	4.33745	n = number of weighing. This can't exceed 50.
2	18722	4.316766	n = 7
3	40322	4.273494	
4	64802	4.224514	
5	74882	4.20378	
6	84962	4.18439	No data entry is required for derived values, which are colored red, such as n and I. These values are tabulated automatically and their cells are protected from alteration. Multiple weighings at a single point in time requires multiple entries in each column. Reenter the time in column **X** and enter the corresponding weight in column **Y**. Enter the time and weight units in the spaces below: Unit of Time = m Unit of Weight = g

This sheet derives the regression equation in the form: $y = b_0 + b_1 x + \epsilon$. The intercept and slope are estimated. The sheet determines whether the intercept (weight estimated for time zero) is significantly different from the observed weight at time zero. It also estimates the uncertainty in the slope estimate and compares this uncertainty with EPA's 1% limit.

STEP 1

Review the estimates of the intercept ($\mathbf{b_0}$), slope of the regression line ($\mathbf{b_1}$), and their confidence limits along with the estimates of variance-covariance matrix (**V**) and the residual error variance (**Var**).
Derivation of the estimated intercept ($\mathbf{b_0}$) and slope ($\mathbf{b_1}$) of the regression line

X'X =	7	292331	**Y'Y** =	127.6972	**95% Confidence Limits**	
	292331	1.91E+10	df =	5	$\mathbf{b_0}$ lower limit =	4.353872
$(\mathbf{X'X})^{-1}$ =	0.396793	-6.1E-06	t(0.95, df) =	2.570578	$\mathbf{b_0}$ upper limit =	4.354935
	-6.1E-06	1.46E-10				
det(**X'X**) =	4.81E+10		$\mathbf{b_0}$ =	4.354403	$\mathbf{b_1}$ lower limit =	-2E-06
X'Y =	29.8946		$\mathbf{b_1}$ =	-2E-06	$\mathbf{b_1}$ lower limit =	-2E-06
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Derivation of the error variance (**Var**) and variance-covariance matrix (**V**)

b'X'Y	=	127.6972		SS(model), 2df
b'X'Y - sum(**Y**)^2 / n	=	0.027619		SS(regression) 1df
(**Y'Y - b'X'Y**)	=	5.38E-07		SS(residual)
Var = (**Y'Y - b'X'Y**) / df	=	1.08E-07		MS(residual), n-2 df
V = Var * $(\mathbf{X'X})^{-1}$	=	4.27E-08	-6.5E-13	
		-6.5E-13	1.57E-17	

STEP 2

Examine the upper and lower limits for the intercept, $\mathbf{b_0}$.

$\mathbf{b_0}$ lower limit =	4.353872	
$\mathbf{b_0}$ upper limit =	4.354935	
$\mathbf{y_0}$ =	4.354206	Conclusion: $\mathbf{y_0}$ is within the confidence limits for the intercept

If y_1 is within the confidence limits for the intercept, proceed to STEP 3. Otherwise, consider removing the first observed weight from the analysis. Re-enter the times and weights. Remember that the first time ($\mathbf{X_0}$) should be zero. This will require adjustment of the other elapsed times. After entering the data, return to STEP 1, above.

STEP 3

Examine the upper and lower limits for the slope, $\mathbf{b_1}$. The limits should differ from the estimate by no more than ±1% of the estimated slope.

($\mathbf{b_1}$ upper - $\mathbf{b_1}$) / $|\mathbf{b_1}|$ =	0.51%	Conclusion: Uncertainty is acceptable.
($\mathbf{b_1}$ lower - $\mathbf{b_1}$) / $|\mathbf{b_1}|$ =	-0.51%	

If the uncertainty is unacceptable, consider collecting additional data. Also, view the **Curve** and **Residual** plots. They may reveal a nonlinear relationship for a portion of the data. The initial measurements may not align with subsequent measurements if the device was in the process of stabilizing or equilibrating during those times. If this is the case, the initial points of the **Residual** chart would appear to be outliers. The residuals with the same sign (all positive or all negative) and their magnitude will likely be greater than the magnitude of subsequent residuals. If this is the case, consider removing the initial points from the computations and re-enter the remaining times and weights with the times adjusted so the first entry has time zero.

If the uncertainty is acceptable, print the **Report** spreadsheet and include it with the certification documentation.

3. Assay Results For Permeation Device

This sheet provides calibration information and assay results, including uncertainty estimates for a permeation device identified as: test data

Test Results

Intercept ($\mathbf{b_0}$), slope ($\mathbf{b_1}$), and their confidence limits

					95% Confidence Limits	
X'X =	7	292331	**Y'Y** =	127.6972		
	292331	1.91E+10	df =	5	$\mathbf{b_0}$ lower limit =	4.353872
$(\mathbf{X'X})^{-1}$ =	0.396793	-6.1E-06	t(0.95, df) =	2.570578	$\mathbf{b_0}$ upper limit =	4.354935
	-6.1E-06	1.46E-10				
det(**X'X**) =	4.81E+10		$\mathbf{b_0}$ =	4.354403	$\mathbf{b_1}$ lower limit =	-2E-06
X'Y =	29.8946		$\mathbf{b_1}$ =	-2E-06	$\mathbf{b_1}$ lower limit =	-2E-06
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Error variance (**Var**) and variance-covariance matrix (**V**).

b'X'Y	=	127.6972		SS(model), 2df
b'X'Y - sum(**Y**)^2 / n	=	0.027619		SS(regression) 1df
(**Y'Y** - **b'X'Y**)	=	5.38E-07		SS(residual)
Var = (**Y'Y** - **b'X'Y**) / df	=	1.08E-07		MS(residual), n-2 df
V = Var * $(\mathbf{X'X})^{-1}$	=	4.27E-08	-6.5451E-13	
		-6.5E-13	1.56725E-17	

Upper and lower limits for the intercept, $\mathbf{b_0}$:

$\mathbf{b_0}$ lower limit = 4.3538722
$\mathbf{b_0}$ upper limit = 4.3549347
$\mathbf{y_0}$ = 4.354206

Upper and lower limits for the slope, $\mathbf{b_1}$:

($\mathbf{b_1}$ upper - $\mathbf{b_1}$) / |$\mathbf{b_1}$| = 0.51%
($\mathbf{b_1}$ lower - $\mathbf{b_1}$) / |$\mathbf{b_1}$| = -0.51%

Estimated rate of weight loss, $\mathbf{b_1}$ = 2.005E-06 g/m