

**APPENDIX "I"**

11/29/94

**Method to Determine Length of Rolling Period  
for Liquid/Liquid Material Balance**

- a. **Applicability.** This method determines the length of the rolling material balance period used in the liquid-liquid material balance test method to measure the overall performance of volatile organic compound (VOC) emission control systems employing carbon adsorbers for solvent recovery as the control device. The rolling balance period obtained from this method is source-specific, taking into account the particular configuration and operating parameters of the emission source (process) and its emission control system. Although the use of the rolling material balance approach may be applied to other types of solvent recovery control devices such as refrigeration, the method herein for determining the appropriate rolling balance period is limited to carbon adsorber-type solvent recovery control devices.
- b. **Summary of Method.** Physical properties and usage are determined for the solvent(s) used in the process, and configuration and operating parameters are identified for the emission source and its emission control system. This information is used to calculate the concentration of VOC in the outlet air of the capture unit, amount of VOC adsorbed on the carbon, maximum VOC loading on the carbon, unmeasured solvent holding capacity of the solvent recovery system, and unmeasured solvent holding capacity of the process unit. These values are then used to calculate the rolling material balance period.
- c. **Definitions.** As used in this Section, all terms not defined herein shall have the meaning given them in the November 15, 1990 Clean Air Act Amendments (CAAA), or in Section 2 of Regulation 24.

"Maximum carbon adsorber holding capacity for solvent,  $V_A$ ," means the quantity of solvent (expressed as volume of liquid solvent) adsorbed on the carbon in all the adsorbent beds of the solvent recovery system that is in adsorption equilibrium with the capture unit outlet air stream under the process operating condition of maximum solvent usage.

"Rolling balance period (RBP)" or "rolling material balance period (RMBP)" means the number of consecutive operating 24-hour material balances,  $N_{MBP}$ , used to determine the quantities of solvent usage and recovery for computation of the recovery efficiency for the emission control system,  $E_R$ .

"Unmeasured process holding capacity for solvent,  $V_p$ ," means the aggregate volume contained within the emission source (process) such as reservoirs, surge tanks, and transfer piping where the volumetric quantity of solvent-bearing liquid varies during process operation and where the quantity of solvent in this volume cannot be reasonably measured or determined as part of the daily solvent material balance around the process and emission control system. For the purpose of this method, the portion of the solvent that remains

continuously filled with liquid under all process operating conditions is not considered part of the unmeasured process holding capacity for solvent.

"Unmeasured solvent recovery system holding capacity for solvent,  $V_R$ ," means the sum of the maximum carbon adsorber holding capacity,  $V_A$ , and the unmeasured solvent recovery system support equipment holding capacity,  $V_S$ .

- d. Procedure. Follow the procedure below and complete the worksheets using configuration and operating data specific to the process unit(s) and VOC emission control system for which the rolling balance period determination is being made.
1. Solvent Properties. The purpose of this step is to determine representative values for the molecular weight and liquid density of the solvent(s) used in the process.
    - i. Single Component Solvent. If a single component solvent (not a mixture) is used exclusively for the process unit(s) served by the emission control system, then record the chemical name of the solvent, its molecular weight, and liquid density in lines 1a, 2, and 3, respectively, of Worksheet A and proceed to 4.2.

$$Y = \sum_{i=1}^n (x_i Y_i) \quad (1)$$

- ii. Multiple Solvent or Solvent Mixtures. If multiple solvents or solvent mixtures are used, complete Worksheet A. List the chemical names of the individual organic compounds, including the major components of the solvent mixtures, in block 1 of Worksheet A. The organic constituents listed should account for at least 90 percent of the total solvent. Use equation (1) to calculate the weighted average molecular weight,  $M_L$ , and liquid density,  $d_L$ , of the solvents used in the process unit(s). Record these values on lines 2 and 3, respectively, of Worksheet A.

where

Y = Weighted average molecular weight ( $M_L$ ) or liquid density ( $d_L$ ).

$y_i$  = Molecular weight ( $M_i$ ) or liquid density ( $d_i$ ) for VOC i.

$x_i$  = Fraction of total solvent for VOC i.

$n$  = Number of VOC species in the solvent(s).

<b>WORKSHEET A SOLVENT DESCRIPTION</b>				
<b>Solvent Composition</b>	<b>Annual Usage (gal/yr)</b>	<b>(100•x<sub>i</sub>) Percent of Total Solvents Listed</b>	<b>(M<sub>i</sub>) Molecular Weight (lb/lb<sub>mole</sub>)</b>	<b>(d<sub>i</sub>) Liquid Density (lb/gal)</b>
1a				
1b				
1c				
1d				
1e				
1f				
1g				
1h				
Total				
2.	Solvent Molecular Weight (weighted average), (M <sub>i</sub> )			lb/lb <sub>mole</sub>
3.	Solvent Liquid Density (weighted average), (d <sub>i</sub> )			lb/lb <sub>mole</sub>

2. Emission Source and Control System Description. In this step, the site-specific system design and operation information needed to determine the appropriate rolling balance period is developed and compiled in Worksheet B. Complete Worksheet B by providing the indicated information specific to the emissionsource process unit(s) and emission control system for which this rolling balance period determination is being made. Unless otherwise specified, the information requested refers to the aggregate of all the process units of the emission source linked to and served by the emission control system containing the carbon solvent recovery control device.
  - i. Number of Process Units. Record the total number of process units (e.g., dip tanks, spray booths) connected to the capture system and manifolded to the solvent recovery control system on line 1 of Worksheet B.
  - ii. Solvent Usage. The maximum daily solvent usage reported on

line 2 of Worksheet B is the maximum total solvent throughput of the process unit(s) that would be used in a day under peak production. The average daily solvent usage requested in line 3 of Worksheet B is the annual total solvent throughput of the process unit(s) divided by the number of days in the year the process unit(s) was in operation.

- iii. Unmeasured Process Holding Capacity for Solvent. Estimate ( $\pm 10$  gallons) the unmeasured solvent holding capacity of each process unit served by the capture and solvent recovery systems in this analysis. Compute the aggregate total unmeasured volume of these process units, and then compare this total to 10 percent of the value listed in Worksheet B, line 3 ( $0.1 \times Q'_{SP}$ ) for the average daily solvent usage. Enter on line 4 the smaller of the values of the estimated aggregate total unmeasured process holding capacity and 10 percent of the average daily solvent usage reported on line 3 of Worksheet B.
  
- iv. Capture System Air Flow Rate. Report on line 5 of Worksheet B the total volumetric air flow rate (adjusted to the standard conditions of 70°F and 1.0 atm) output from the capture system to the solvent recovery system.

<b>WORKSHEET B</b>	
<b>EMISSION SOURCE AND CONTROL SYSTEM DESCRIPTION</b>	
<b>Emission Source - Process Units</b>	
1.	Number of Process Units
2.	Maximum Daily Solvent Usage, $Q_{SP}$ <span style="float: right;">gal/day</span>
3.	Average Daily Solvent Usage, $Q'_{SP}$ <span style="float: right;">gal/day</span>
4.	Unmeasured Solvent Holding Capacity In Process, $V_P$ <span style="float: right;">gal<sup>a</sup></span>
<b>Emission Control System - Capture Unit</b>	
5.	Average Air Flow Rate, $G_{CU}$ <span style="float: right;">scfm<sup>b</sup></span>
6.	Maximum VOC Concentration In Outlet Air, $C_O$ <span style="float: right;">ppmv</span>
<b>Emission Control System - Solvent Recovery Control Unit</b>	
7.	Number of Carbon Beds

8.	Total Carbon in Solvent Recovery Unit, $W_C$	lb
9.	Maximum Solvent Loading On Carbon, $V_A$	gal
10.	Unmeasured Capacity In Support Equipment, $V_S$	gal
11.	Total Unmeasured Capacity, $V_R = V_A + V_S$	gal

<sup>a</sup>Maximum value limited to 10 percent of the value in line 3, ( $Q'_{SP}$ ).

<sup>b</sup>Standard conditions: 70°F and 1.0 atm.

- v. Maximum VOC Concentration in Capture System Outlet. Use equation (2) to estimate the maximum concentration of VOC in the outlet air stream of the capture unit (inlet air stream to the carbon adsorber beds of the solvent recovery control unit). If actual VOC concentrations (measured on the same capture unit under the current operating conditions within the past 2 years using an EPA approved test method) are available and their average exceeds the concentration calculated in equation (2), then record the average of the measured concentrations on Worksheet B, line 6; otherwise record the concentration from equation (2) on line 6.

$$C_O = 2.69 \times 10^5 \left( \frac{Q_{SP} d_L}{M_{LGR}} \right) \quad (2)$$

where

$C_O$  = Concentration of VOC in outlet air of capture unit, ppmv.

$Q_{SP}$  = Maximum daily solvent throughput to the process units, gal/day (Worksheet B, line 2).

$d_L$  = Solvent liquid density, lb/gal (Worksheet A, line 3).

$M_L$  = Solvent molecular weight, lb/lb<sub>mole</sub> (Worksheet A, line 2).

$G_{CU}$  = Capture unit outlet air flow rate, scfm (Worksheet B, line 5).

- vi. Quantity of Carbon in Solvent Recovery System. Report the number of carbon adsorber beds (both online and offline for regeneration) in the solvent recovery system on line 7 of Worksheet B. Determine the total mass of carbon in the solvent recovery system by summing the masses in each of the carbon adsorber beds, and enter the total on line 8 of Worksheet B.
- vii. Maximum Solvent Loading on the Carbon. To estimate the maximum solvent loading (i.e., solvent holding capacity) for the total carbon in the solvent recovery control unit, use equations (3) and (4). Record the value calculated for  $V_A$  in equation (4) on line 9 of Worksheet B.

$$W_A = \exp(Y) \quad (3)$$

where

$$Y = \sum_{j=1}^3 (b_j X_j)$$

$$X = \ln(C_0)$$

$$b_0 = -3.047598$$

$$b_1 = 0.275410$$

$$b_2 = -0.003271$$

$$b_3 = -0.000486$$

$C_0$  = Maximum VOC concentration in capture unit outlet air, ppmv (Worksheet B, line 6).

$W_A$  = Amount of VOC adsorbed on the carbon, lb VOC/lb carbon.

$$V_A = \left\{ \frac{W_A W_C}{d_L} \right\} \quad (4)$$

where

- $V_A$  = Maximum solvent loading on the carbon in the solvent recovery unit, gal.
- $W_A$  = Amount of VOC adsorbed on the carbon (equation (3)).
- $W_C$  = Total quantity of carbon in the solvent recovery unit, lb carbon (Worksheet B, line 3).
- $d_L$  = Solvent liquid density, lb/gal (Worksheet A, line 3).

viii. Unmeasured Solvent Capacity in Support Equipment. In addition to the solvent adsorbed on the carbon, the solvent recovery system may contain time-varying quantities of solvent in its support equipment such as condensate tanks, decanters, and surge/collection tanks, which are not measured as part of the daily material balance. Estimate that portion of the volume in the support equipment over which the unmeasured quantity of solvent it contains may vary between material balances. Do not include the capacity where the solvent inventory remains essentially constant over time. Compare this estimated value of the unmeasured solvent holding capacity in the support equipment with the value corresponding to 10 percent of the average daily solvent usage (Worksheet B, line 3), and record the smaller of these two values as  $V_S$  on line 10 of Worksheet B.

ix. Unmeasured Solvent Capacity for Solvent Recovery System. The unmeasured solvent holding capacity of the solvent recovery system is the sum of the maximum solvent loading on the carbon and the unmeasured holding capacity of the support equipment. On Worksheet B, sum the values on lines 9 and 10 and record this sum on line 11.

e. Data Analysis and Calculations. Rolling Material Balance Period Determination. Use equation (5) and the values of the indicated variables from Worksheet B to compute the appropriate rolling balance period (number of consecutive 24-hour operating period material balances) for this specific emission source and emission control system.

$$N_{RBP} = \begin{cases} 1, & \text{if } \exp(D) < 1 \\ \text{integer}(\exp(D)), & \text{if } 1 \leq \exp(D) \leq 30 \\ 30, & \text{if } \exp(D) > 30 \end{cases} \quad (5)$$

where

$$D = b_0 + \sum_{j=1}^{12} (b_j X_j)$$

$$b_0 = 2.36877 \times 10^0$$

$$b_1 = -9.47906 \times 10^{-2}$$

$$b_2 = -7.22840 \times 10^{-3}$$

$$b_3 = 2.22034 \times 10^{-4}$$

$$b_4 = 1.22762 \times 10^{-1}$$

$$b_5 = 1.48939 \times 10^{-2}$$

$$b_6 = -1.77705 \times 10^{-3}$$

$$b_7 = 1.43241 \times 10^0$$

$$b_8 = -3.77860 \times 10^{-1}$$

$$b_9 = 7.89384 \times 10^{-4}$$

$$b_{10} = 3.76158 \times 10^{-2}$$

$$b_{11} = -1.05375 \times 10^{-1}$$

$$b_{12} = 8.57476 \times 10^{-4}$$

$$X_1 = (0.001 \times Q_{SP})$$

$$X_2 = (X_1)^2$$

$$X_3 = (X_1)^3$$

$$X_4 = (0.001 \times V_R)$$

$$X_5 = (X_4)^2$$

$$X_6 = (X_4)^3$$

$$X_7 = (0.001 \times V_P)$$

$$X_8 = (X_7)^2$$

$$X_9 = (X_1 \times X_4)$$

$$X_{10} = (X_1 \times X_7)$$

$$X_{11} = (X_4 \times X_7)$$

$$X_{12} = (X_1 \times X_4 \times X_7)$$

$N_{RBP}$  = Rolling balance period, days.

$Q_{SP}$  = Maximum daily solvent throughput to the process units, gal/day (Worksheet B, line 2).

$V_R$  = Unmeasured solvent holding capacity of the solvent recovery system, gal (Worksheet B, line 11).

$V_P$  = Unmeasured solvent holding capacity of the process units, gal (Worksheet B, line 4).