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- If the combustion effluent contains an excess of air Y% over the stoichiometric requirement, the moles of oxygen in the combustion effluent are:

$$S \times Y/100 \text{ moles } O_2/100 \text{ g herbicide} \qquad (2)$$

- The nitrogen content of the product gas follows directly from the composition of feed air, i.e.,

$0.7809S/0.2095$ moles N_2 from oxygen requirement

and

$0.7809S\ Y/(0.2095 \times 100)$ moles N_2 present in the excess air or

$$(0.7809S/0.2095)(1 + Y/100) \text{ moles } N_2 \text{ per 100 g herbicide} \tag{3}$$

where 0.7809 and 0.2095 are the fractional composition of N_2 and O_2, respectively, in a standard dry atmosphere.

- On a dry basis, the moles of combustion effluent produced per 100 g herbicide are

$$\begin{aligned} &C/12.011 + C\ell/35.453 + SY/100 \\ &\quad + (0.7809S/0.2095)(1 + Y/100) \end{aligned} \tag{4}$$

- The stoichiometric air flow requirement per 100 g herbicide is

$$S/0.2095 \text{ moles } = K'$$

Now, one mole of dry gas occupies 0.02406 m^3 at 20°C. The derivation up to this point has been based on 100 g herbicide. A waste feed of W metric tons per hour is W x $10^6/100$ or W x 10^4 times greater than 100 g. Thus, the stoichiometric air flow rate requirement in dry m^3/hr for W metric tons per hour of herbicide is:

$$240.6S\ W/0.2095\ m^3/hr \text{ at } 20^\circ C \tag{5}$$

- By definition, from Equation (2), the fraction of excess air is

$$Y/100 = \frac{\text{air flow - stoichiometric air flow}}{\text{stoichiometric air flow}}$$

or

$$Y/100 = (A - 240.6S\ W/0.2095)/(240.6S\ W/0.2095)$$

$$Y/100 = (0.2095A/240.6SW) - 1$$

Therefore,

$$1 + Y/100 = 0.2095A/240.6SW$$

- Equation (4) becomes

$$\frac{C}{12.011} + \frac{C\ell}{35.453} + \left(\frac{0.2095A}{240.6SW} - 1\right) S + \frac{0.7809S}{0.2095}\left(\frac{0.2095A}{240.6SW}\right) \text{moles/hr}$$

- Thus the total flow of combustion effluent per incinerator in dry moles/hr at 20°C for W metric tons per hour herbicide feed is

$$P = [C/12.011 + C\ell/35.453 + (A/240.6W) - S]\ 10^4W$$

- Substituting for S from Equation (1) and collecting terms

$$\begin{aligned} P &= \left[\frac{A}{240.6W} + \frac{C\ell}{35.453} - \frac{1}{4}\left(\frac{H}{1.008} - \frac{C\ell}{35.453}\right) + \frac{0}{32}\right] 10^4W \\ &= A + 240.6W\ (0132 + C\ell/28.362 + H/4.032)\ m^3/hr \end{aligned} \qquad (6)$$

- Total 2,4-D + 2,4,5-T fed is Wa metric tons/hour

  Total 2,4-D + 2,4,5-T emitted is Pb metric tons/hour

  Total TCDD fed is Wd metric tons/hour

  Total TCDD emitted is Pe metric tons/hour

- The destruction efficiency (DE) for 2,4-D + 2,4,5-T is

$$DE = \frac{Wa - Pb}{Wa} \times 100$$

or

$$DE - \left(1 - \frac{P}{W}\ \frac{b}{a}\right) \times 100 \qquad (7)$$

$$Y = \frac{\%\ O_2 - 0.5\%\ CO}{0.264\%\ N_2 - (\%\ O_2 - 0.5\%\ CO)} \qquad (11)$$

Since CO in the combustion effluent is very small (ppm concentrations compared to percent concentrations for O_2 and N_2),

$$Y \cong \%\ O_2/(0.264\%\ N_2 - \%\ O_2) \qquad (12)$$

- The percentage of nitrogen can be inferred as the balance of the product stream after O_2 and CO_2 are measured and HCℓ is calculated, i.e.,

$$\%\ N_2 = 100 - \%\ O_2 - \%\ CO_2 - \%\ HC\ell - \%\ CO - \%\ \text{hydrocarbons}$$

Now, CO and hydrocarbons are trace quantitites, so

$$\% N_2 \cong 100 - \% O_2 - \% CO_2 - \% HC\ell \qquad (13)$$

- The HCℓ content of the combustion effluent can be deduced from the carbon-to-chlorine ratio in the herbicide because all but trace quantities of Cℓ go to HCℓ and all but trace quantities of C go to CO_2 product. Since

$$\% HC\ell = (C\ell/C)\ \% CO_2$$

then, substituting into Equation (13)

$$\% N_2 \cong 100 - \% O_2 - (1 + C\ell/C)\ \% CO_2 \qquad (14)$$

- Therefore, excess air, Y, is obtained from Equations (12) and (14)

$$Y = \% O_2/[0.264\ (100 - \% O_2 - (1 + C\ell/C)\ \% CO_2) - \% O_2] \qquad (15)$$

or

$$Y = \% O_2/[26.4 - 1.264\% O_2 - 0.264\ (1 + C\ell/C)\ \% CO_2] \qquad (16)$$

- Substituting into Equation (10) the expression for Y from Equation (16) and the expression for S in Equation (1), gives

$$DE/100 = \Bigg[1 - \frac{240.6b}{a}\Bigg(K' \cdot \Bigg(1 + \frac{\% O_2}{100\ (26.4 - 1.264\% O_2 - 0.264\ (1 + C\ell/C)\% CO_2}\Bigg) + K\Bigg)\Bigg] \qquad (17)$$

where

$$K' = \frac{(C/12.011 + (1/4)\ (H/1,008 - C\ell/35,453) - O/32}{0.2095}$$

and

$$K = O/32 + C\ell/28.362 - H/4.032$$

- Now, the quantities K and K' can be assumed to be second-order variations related to the herbicide composition because of the similarity in composition of 2,4-D and 2,4,5-T in the waste. They are neglected. Variances in the $C\ell/C$ ratio, used in the % N_2 calculation, Equation (14), are of more concern because of the magnitude of the N_2 content in the combustion effluent. Variance in the $C\ell/C$ ratio must be considered if the herbicide is diluted subsequent to the determination of a (the weight fraction of 2,4-D + 2,4,5-T in herbicide). This is especially true if the diluent is quite different in composition from the herbicide, such as the diesel fuel used to rinse drums and other equipment involved in loading herbicide on the ship.

- Equation (17) is the final expression for the destruction efficiency of 2,4-D + 2,4,5-T. A similar expression results for the destruction efficiency of TCDD by substituting d for a and e for b, where d and e are, respectively, the weight fraction of TCDD in the herbicide and the emission rate of TCDD in the combustion effluent.

- The variation in DE/100 can be approximated in the region of the average values for the variables O_2, CO_2, $C\ell/C$, a, b, d, and e by Taylor's expansion. Thus, for the variance in destruction efficiency for 2,4-D + 2,4,5-T

$$V\,(DE/100) = \left(\frac{\partial\,(DE/100)}{\partial a}\right)^2 V(a) + \left(\frac{\partial\,(DE/100)}{\partial b}\right)^2 V(b) + \left(\frac{\partial\,(DE/100)}{\partial\,(C\ell/C)}\right)^2 V(C\ell/C) + \left(\frac{\partial\,(DE/100)}{\partial\,O_2}\right)^2 V(O_2) + \left(\frac{\partial\,(DE/100)}{\partial\,CO_2}\right)^2 V(CO_2) \qquad (18)$$

The variance in destruction efficiency for TCDD is obtained by substituting d for a and e for b in Equation (18).

- Approximate expressions for the partial derivatives in Equation (18) are

$$\frac{\partial\ (DE/100)}{\partial a} = \frac{240.6b}{a^2}$$

$$\left[K'\left(1 + \frac{\%\ O_2}{100\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2}\right) + K\right] \tag{19}$$

$$\frac{\partial\ (DE/100)}{\partial b} = \frac{-240.6}{a}$$

$$\left[K'\left(1 + \frac{\%\ O_2}{100\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2}\right) + K\right] \tag{20}$$

$$\frac{\partial\ (DE/100)}{\partial\ (C\ell/C)} = \frac{-240.6b\ K'\ \%\ O_2\ (0.264\%\ CO_2)}{100a\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2)^2} \tag{21}$$

$$\frac{\partial\ (DE/100)}{\partial\ (\%\ O_2)} = \frac{-240.6b\ K'}{a}$$

$$\times \left[\frac{26.4 \times 100 + 26.4\ (1 + C\ell/C)\ \%\ CO_2}{(1/\%\ O_2)^2\ [(1/\%\ O_2)(26.4 \times 100\ (1 + C\ell/C)\ \%\ CO_2) - 126.4]^2}\right] \tag{22}$$

$$\frac{\partial\ (DE/100)}{\partial\ (\%\ CO_2)} = -\frac{240.6b\ K'\ \%\ O_2\ (0.264\ C\ell/C)}{100a\ (26.4 - 1.264\%\ O_2 - 0.264\ (1 + C\ell/C)\ \%\ CO_2)^2} \tag{23}$$

The variances in d and e are obtained by substituting d for a and e for b in Equations (19) through (23).

- The means and variances of the variables in Equations (19) through (23) are obtained as follows.

1) V(a), variance in weight percent of 2,4-D and 2,4,5-T in herbicide

From data presented in Table 11 giving the composition of four Gulfport lots of herbicide, the mean and standard deviation in the total of 2,4-D and 2,4,5-T in the herbicide were calculated to be

$$\bar{a} = 0.8599\%$$

$$s_a = 0.0547\%$$

2) V(b), variance in emission concentration of 2,4-D and 2,4,5-T

From data presented in Table 51 giving the emission concentrations of 2,4-D and 2,4,5-T calculated from analyses at TRW, the mean and standard deviation emission concentration of 2,4-D + 2,4,5-T were calculated to be

$$\bar{b} = 46.7\ \mu g/m^3 = 46.7 \times 10^{-12} \text{ metric tons/m}^3$$

$$s_b = 72.2\ \mu g/m^3 = 72.2 \times 10^{-12} \text{ metric tons/m}^3$$

3) V(d), variance in TCDD content of herbicide

The mean and standard deviation in TCDD content of the herbicide were calculated from data presented in Table 50.

$$\bar{d} = 1.916 \times 10^{-6}$$

$$s_d = 7,238 \times 10^{-7}$$

4) V(e), variance in emission concentration of TCDD

Table 50 presents emission concentrations of TCDD calculated from the WSU analyses. The mean and standard deviation are

$$\bar{e} = 186\ ng/m^3 = 1.86 \times 10^{-13} \text{ metric tons/m}^3$$

$$s_e = 142\ ng/m^3 = 1.42 \times 10^{-13} \text{ metric tons/m}^3$$

5) $V(C\ell/C)$, variance in chlorine-to-carbon ratio in waste

After drums containing herbicide were drained, they were rinsed. During Johnston Island dedrumming operations, drums averaged 50 gallons of herbicide, and drum rinses averaged 2 ±0.3 gallons of diesel fuel. The carbon content of diesel fuel was taken as 84.9% and its specific gravity as 0.778. From Table 8, the carbon and chlorine contents of the herbicide were 49.11 and 29.87%, respectively. From these data, the ±2s range for the $C\ell/C$ ratio is 0.5798 to 0.5870. Therefore,

$$\overline{C\ell/C} = 0.5834$$

$$s_{C\ell/C} = 0.0018$$

6) $V(O_2)$ variance in oxygen content of combustion effluent

Table 16 presents gas composition data for all three burns. From these data, the average and standard deviation of $\%\ O_2$ were calculated:

$$\%\ \overline{O_2} = 8.9$$

$$s_{\%\ O_2} = 1.4$$

7) $V(CO_2)$, variance in carbon dioxide content of combustion effluent

From data presented in Table 16, the average and standard deviation at $\%\ CO_2$ were calculated:

$$\%\ \overline{CO_2} = 10.3$$

$$s_{\%\ CO_2} = 1.7$$

8) Values for K and K' were obtained from the average herbicide composition. From Table 8,

carbon = 49.11%

chlorine = 29.87%

oxygen = 16.37%

hydrogen = 4.65%

$$K = 16.37/32 + 29.87/28.362 - 4.65/4.032 = 0.4114$$

$$K' = \frac{(49.11/12.011 + 4.65/4.032 - 5.974/28.362 - 16.37/32)}{0.2095}$$

$$= 21.5744$$

- In summary, the values needed to solve Equations (17) through (23) are given in Table 56.

TABLE 56. SUMMARY OF ERROR ANALYSIS VARIANCES

	Variable	Units	Mean	Standard Deviation	$\left[\frac{\partial(DE/100)}{\partial(\text{Variable})}\right]^2$	
					2,4-D+2,4,5-T	TCDD
a	Weight fraction 2,4-D + 2,4,5-T in herbicide	dimensionless	0.8599	0.0547	1.13×10^{-13}	---
b	Emission concentration of 2,4-D + 2,4,5-T	metric ton/m^3	4.67×10^{-11}	7.22×10^{-11}	$3.85\times10^{+7}$	---
d	Weight fraction TCDD in herbicide	dimensionless	1.916×10^{-5}	7.23×10^{-7}	---	$7.30\times10^{+4}$
e	Emission concentration of TCDD	metric ton/m^3	1.859×10^{-13}	1.42×10^{-13}	---	$7.75\times10^{+18}$
Cl/C	Chlorine/carbon ratio in waste	dimensionless	0.5834	0.0018	3.36×10^{-19}	1.07×10^{-12}
$\%O_2$	Oxygen content of combustion effluent	percent	8.9	1.4	7.05×10^{-18}	1.12×10^{-22}
$\%CO_2$	Carbon dioxide content of combustion effluent	percent	10.3	1.7	1.08×10^{-21}	3.45×10^{-15}
K	Second order variable	moles	0.4144	---	---	---
K'	Second order variable	moles	21.57	---	---	---

2. MEAN AND VARIANCE OF DESTRUCTION EFFICIENCIES

2.1 2,4-D and 2,4,5-T

- Solving Equation (18) with the values in Table 56, the variance and standard deviation of (DE/100) of 2,4-D + 2,4,5-T are:

$$V\ (DE/100) = 2.009 \times 10^{-13}$$

$$s\ (DE/100) = 4.482 \times 10^{-7}$$

- From Equation (17), the mean destruction efficiency for 2,4-D + 2,4,5-T is

$$\overline{DE}/100 = 0.99999971$$

- It is assumed that calculations of destruction efficiency are normally distributed. The question asked is what percent of a group of destruction efficiency calculations will be less than some specified value and what degree of confidence is there in that estimate of the percentage.

  There are three values for emission rates of 2,4-D + 2,4,5-T given in Table 51. Safety considerations dictate consideration of destruction efficiencies less than some specified value. This value is defined as the one-sided tolerance limit. The value for the one-sided tolerance factor was selected(1) for the population of three analyses such that there would be 95% confidence that not more than 0.1% of 2,4-D + 2,4,5-T destruction efficiencies would be less than the tolerance limit. In other words, the tolerance limit is such that there is 95% confidence that only one 2,4-D + 2,4,5-T destruction efficiency in 1000 would be smaller in value.

  $K = 13.86$, one-sided tolerance factor for $n = 3$ at 95% confidence

  The tolerance limit is

$$\overline{DE}/100 - sK = 0.99999971 - 13.86 \times 4.482 \times 10^{-7}$$

$$= 0.9999935$$

- Therefore, this conservative statistical analysis shows that there is 95% confidence that not more than 1 measured destruction efficiency in 1000 would be less than 99.99935%.

2.2 TCDD

- Solving Equation (18) with the values in Table 56, the variance and standard deviation of (DE/100) of TCDD are:

$$V(DE/100) = 1.944 \times 10^{-7}$$

$$s(DE/100) = 4.409 \times 10^{-4}$$

- From Equation (17) the mean destruction efficiency for TCDD is

$$DE/100 = 0.99948$$

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1. "Handbook of Statistical Tables," D.B. Owen, Addison-Wesley, New York, p. 117, 1962.

- It is assumed that calculations of destruction efficiency for TCDD are normally distributed. The questions asked is what percentage of a group of dioxin destruction efficiency calculations will be less than some specified value and what degree of confidence is there in that estimate of the percentage.

  There are four values for emission rates of TCDD given in Table 50. Safety considerations dictate consideration of destruction efficiencies less than some specified value. This value is defined by the one-sided tolerance limit. The value for the one-sided tolerance factor was selected(1) for the population of four analyses such that there would be 95% confidence that not more than 0.1% of TCDD destruction efficiencies would be less than the tolerance limit. In other words, the tolerance limit is such that there is 95% confidence that only one TCDD destruction efficiency in 1000 would be smaller in value.

  $K = 9.21$, one-sided tolerance factor for $n = 4$
  at 95% confidence

  The tolerance limit is

  $$\overline{DE}/100 - sK = 0.99948 - 9.21 \times 4.409 \times 10^{-4}$$

  $$= 0.9954$$

- Therefore, this conservative statistical analysis shows that there is 95% confidence that not more than 1 measured destruction efficiency for TCDD in 1000 would be less than 99.54%.