

APPENDIX N

SAMPLE EXPERIMENTAL ERROR ANALYSIS

Let A_j be the peak area of GC analysis for the species j

in the gaseous product, in arbitrary unit,

f_j be the TCD weight response factor of GC analysis for
the species j ,

F_i^o be the mass flow rate of component i in the feed, in
 $\frac{\text{g}}{\text{hr}}$,

G be the mass flow rate of gaseous product, in $\frac{\text{g}}{\text{hr}}$,

M_i be the molecular weight of species i ,

in $\frac{\text{g}}{\text{g-mol}}$,

n_i be the moles of species i in gaseous product generated
per hour, in $\frac{\text{g-mol}}{\text{hr}}$,

n_i^o be the molar flow rate of component i in the feed,

in $\frac{\text{g-mol}}{\text{hr}}$,

r be the net reaction rate in terms of the sum of three
component rates (H_2 , CO and C_2H_4), in $\frac{\text{g-mol}}{\text{g cat-hr}}$,

$$r \equiv r_{\text{H}_2} + r_{\text{CO}} + r_{\text{C}_2\text{H}_4} \quad (\text{N.1})$$

r_i be the rate of species i , in $\frac{\text{g-mol } i}{\text{g cat-hr}}$,

w be the mass of catalyst used, in g,

ϵ be the experimental error of the net reaction rate,

in $\frac{\text{g-mol}}{\text{g cat-hr}}$,

and ϵ_i be the experimental error of i component rate, in

$\frac{\text{g-mol } i}{\text{g cat-hr}}$.

Following the discussion in V-4, for a differential reactor, the component rate r_i can be interpreted directly from the Eqn. (5.1) which is equivalent to the equation below:

$$r_i = \frac{1}{w} (n_i^o - n_i) \quad (\text{N.2})$$

$$= \frac{1}{wM_i} \left[F_i^o - G \left(\frac{f_i A_i}{\sum_{j=1}^6 f_j A_j} \right) \right] \quad (\text{N.3})$$

Therefore, each component rate is a function of following independent variables: A_j ($j = 1$ to 6), f_j ($j = 1$ to 5),

F_i^o , G , and w .

Let δ_k denotes the uncertainty for the independent variable k ,

then the experimental error for the component rate can be calculated from the equation below:

$$\epsilon_i = \left[\left(\frac{\partial r_i}{\partial F_i^o} \delta_{F_i^o} \right)^2 + \left(\frac{\partial r_i}{\partial G} \delta_G \right)^2 + \sum_{j=1}^5 \left(\frac{\partial r_i}{\partial f_j} \delta_{f_j} \right)^2 + \sum_{j=1}^6 \left(\frac{\partial r_i}{\partial A_j} \delta_{A_j} \right)^2 + \left(\frac{\partial r_i}{\partial w} \delta_w \right)^2 \right]^{\frac{1}{2}} \quad (N.4)$$

The partial derivatives are derived as follows:

$$\frac{\partial r_i}{\partial F_i^o} = \frac{1}{wM_i} \quad (N.5)$$

$$\frac{\partial r_i}{\partial G} = - \frac{1}{wM_i} \left(\frac{f_i A_i}{\sum_{j=1}^6 f_j A_j} \right) \quad (N.6)$$

$$\frac{\partial \lambda_i}{\partial f_j} = - \frac{G}{\omega M_i} \left[\frac{A_i}{\sum_{j=1}^6 f_j A_j} - \frac{f_i A_i^2}{(\sum_{j=1}^6 f_j A_j)^2} \right]$$

$$\text{for } j = i \quad (N.7)$$

$$\frac{\partial \lambda_i}{\partial f_j} = - \frac{G}{\omega M_i} \left[- \frac{f_i A_i A_j}{(\sum_{j=1}^6 f_j A_j)^2} \right] \text{ for } j \neq i \quad (N.8)$$

$$\frac{\partial \lambda_i}{\partial A_j} = - \frac{G}{\omega M_i} \left[\frac{f_i}{\sum_{j=1}^6 f_j A_j} - \frac{f_i^2 A_i}{(\sum_{j=1}^6 f_j A_j)^2} \right]$$

$$\text{for } j \neq i \quad (N.9)$$

$$\frac{\partial \lambda_i}{\partial A_j} = - \frac{G}{\omega M_i} \left[- \frac{f_i f_j A_i}{(\sum_{j=1}^6 f_j A_j)^2} \right] \text{ for } j \neq i \quad (N.10)$$

$$\frac{\partial \lambda_i}{\partial \omega} = - \frac{1}{\omega^2 M_i} \left[F_i^0 - G \left(\frac{f_i A_i}{\sum_{j=1}^6 f_j A_j} \right) \right] \quad (N.11)$$

Following data were taken from Run #03314,

$$F_{H_2}^o = 1.08 \pm 0.06 \text{ g-mol/hr,}$$

$$F_{CO}^o = 18.67 \pm 1.15 \text{ g-mol/hr,}$$

$$F_{C_2H_4}^o = 7.51 \pm 0.05 \text{ g-mol/hr,}$$

$$F_{CO_2}^o = 30.57 \pm 0.11 \text{ g-mol/hr,}$$

$$F_{CH_4}^o = 6.21 \pm 0.05 \text{ g-mol/hr,}$$

$$G = 40.20 \pm 2.06 \text{ g/hr,}$$

$$w = 1.00 \pm 0.001 \text{ g,}$$

$$f_{H_2} = 0.0535 \pm 0.0028,$$

$$f_{CO} = 0.5849 \pm 0.0295,$$

$$f_{C_2H_4} = 0.2694 \pm 0.0131,$$

$$f_{CH_4} = 0.2908 \pm 0.0123,$$

$$f_{C_2H_6} = 0.2707 \pm 0.0012,$$

$$A_{H_2} = 29.91 \pm 1.89,$$

$$A_{CO} = 62.63 \pm 2.78,$$

$$A_{C_2H_4} = 39.42 \pm 2.48,$$

$$A_{CO_2} = 53.43 \pm 2.87,$$

$$A_{\text{CH}_4} = 33.01 \pm 1.89,$$

$$A_{\text{C}_2\text{H}_6} = 0.99 \pm 0.05.$$

The molecular weights used in the calculation are:

$$M_{\text{H}_2} = 2.016,$$

$$M_{\text{CO}} = 28.010,$$

$$M_{\text{C}_2\text{H}_4} = 28.054,$$

$$M_{\text{CO}_2} = 44.010,$$

$$M_{\text{CH}_4} = 16.043,$$

$$M_{\text{C}_2\text{H}_6} = 30.070.$$

Plugging all values into Eqn. (N.3) and then Eqn. (N.1) gives

$$r_{\text{H}_2} = 0.2512 \text{ g-mol/g cat-hr},$$

$$r_{\text{CO}} = 0.1994 \text{ g-mol/g cat-hr},$$

$$r_{\text{C}_2\text{H}_4} = 0.1333 \text{ g-mol/g cat-hr},$$

$$\text{and } r = 0.5839 \text{ g-mol/g cat-hr}.$$

Substituting all values of F_i^o , G , W , M_i , f_i , A_j and δ_k into Eqns. (N.5) through (N.11), and finally Eqn. (N.4) results in

$$\epsilon_{H_2}^2 = 0.0017 \text{ (g-mol/g cat-hr)}^2,$$

$$\epsilon_{H_2} = 0.0416 \text{ g-mol/g cat-hr},$$

$$\epsilon_{CO}^2 = 0.0029 \text{ (g-mol/g cat-hr)}^2,$$

$$\epsilon_{CO} = 0.0540 \text{ g-mol/g cat-hr},$$

$$\epsilon_{C_2H_4}^2 = 0.0002 \text{ (g-mol/g cat-hr)}^2,$$

$$\text{and } \epsilon_{C_2H_4} = 0.0130 \text{ g-mol/g cat-hr}.$$

To calculate the uncertainty for the net reaction, use the equation below:

$$\begin{aligned} \epsilon_r &= \left[\left(\frac{\partial r}{\partial n_{H_2}} \epsilon_{H_2} \right)^2 + \left(\frac{\partial r}{\partial n_{CO}} \epsilon_{CO} \right)^2 + \left(\frac{\partial r}{\partial n_{C_2H_4}} \epsilon_{C_2H_4} \right)^2 \right]^{\frac{1}{2}} \\ &= \left(\epsilon_{H_2}^2 + \epsilon_{CO}^2 + \epsilon_{C_2H_4}^2 \right)^{\frac{1}{2}} \end{aligned} \quad (N.12)$$

Substituting the values of $\epsilon_{H_2}^2$, ϵ_{CO}^2 , and $\epsilon_{C_2H_4}^2$ into

Eqn. (N.12) produces the uncertainty for the overall reaction rate of the modified Fischer-Tropsch synthesis, $\epsilon_{\eta} = 0.0693$ g-mol/g cat-hr, which is equivalent to 11.87 % of experimental error.

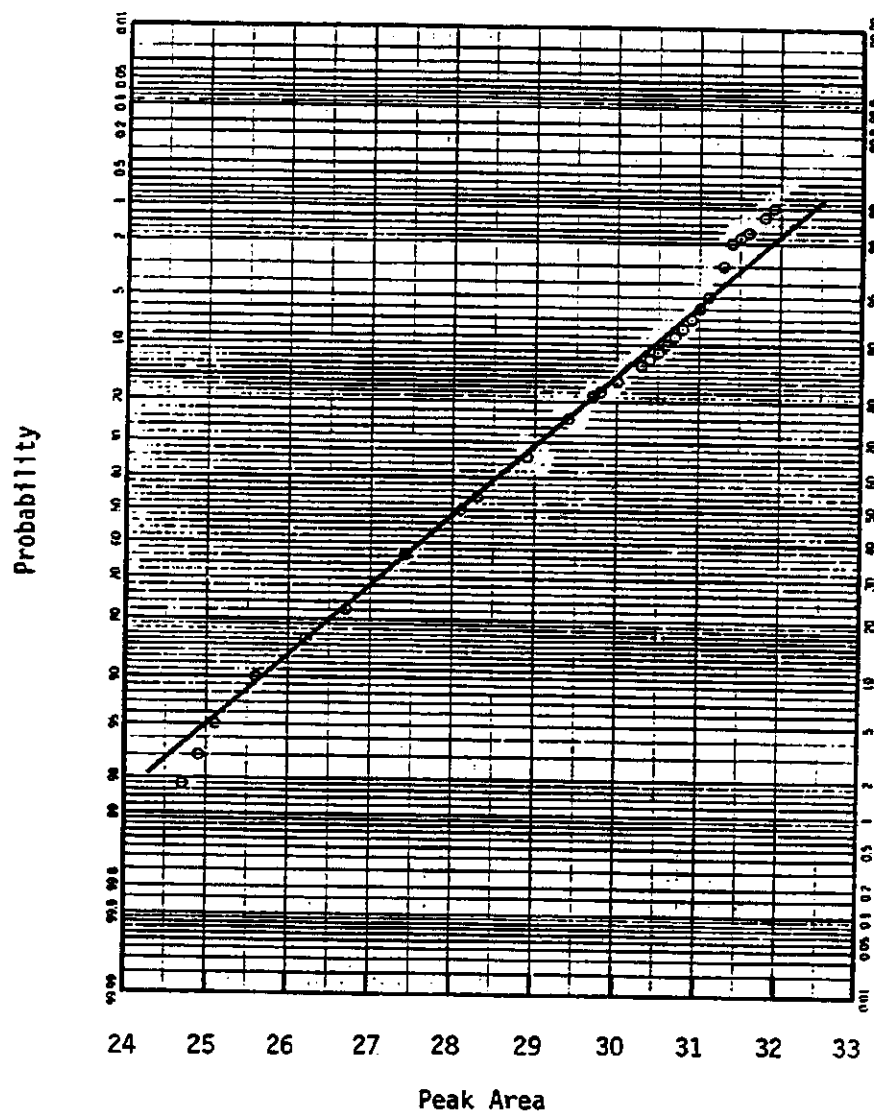


Figure N.1. Experimental Error Distribution of GC Analysis
in Terms of Measured H_2 Peak Area.

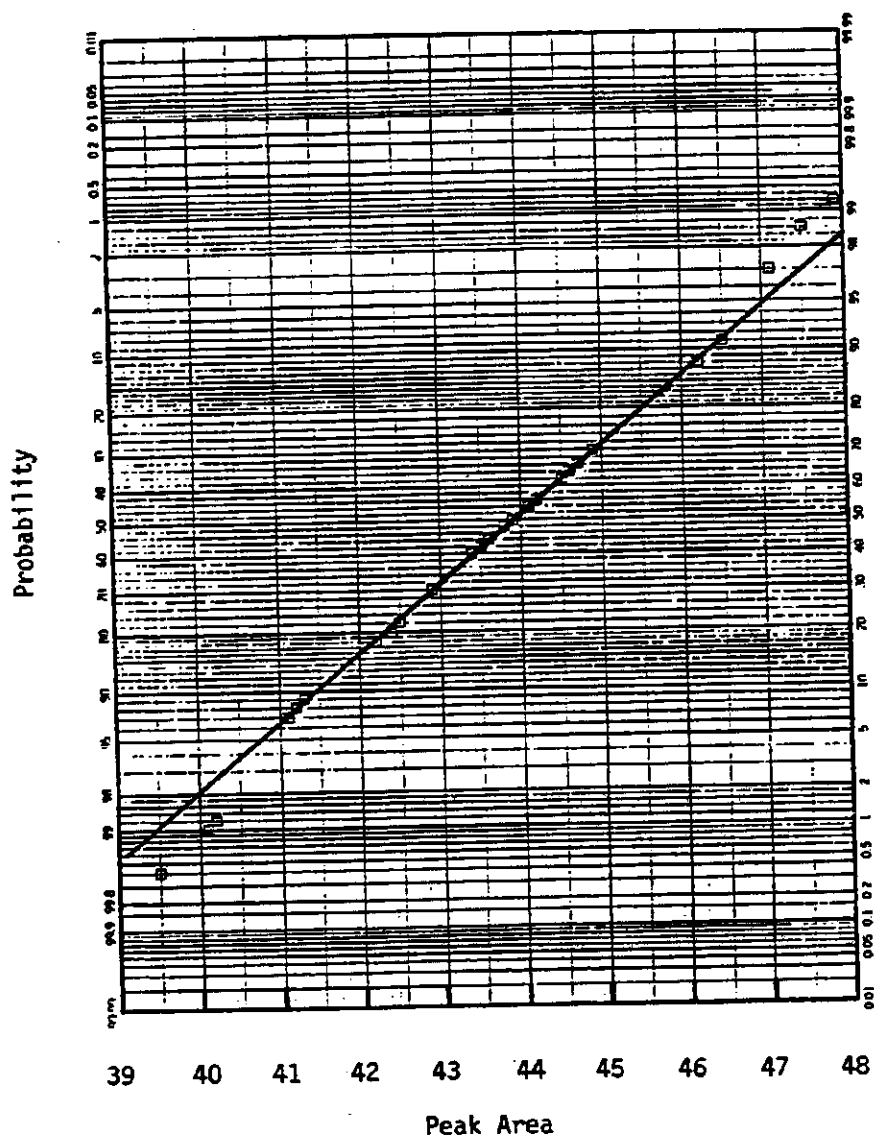


Figure N.2. Experimental Error Distribution of GC Analysis
in Terms of Measured CO Peak Area.

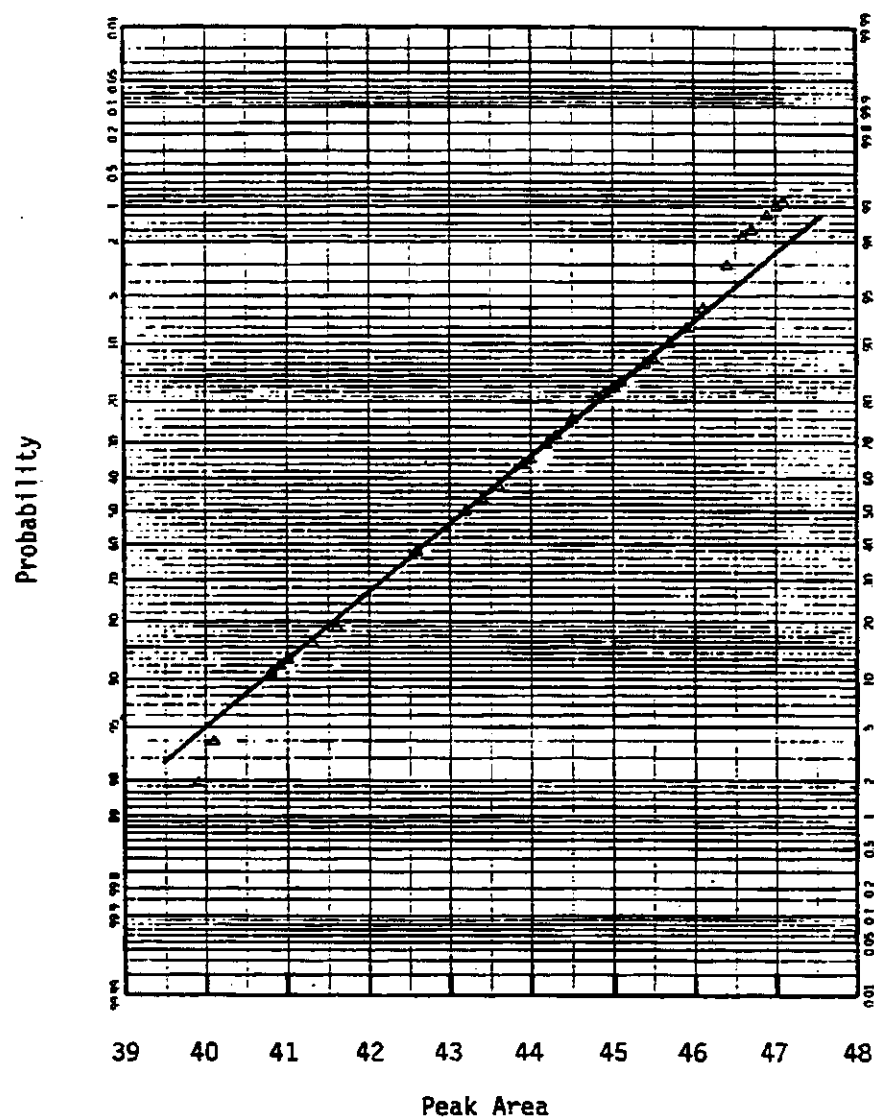


Figure N.3. Experimental Error Distribution of GC Analysis
in Terms of Measured C_2H_4 Peak Area.

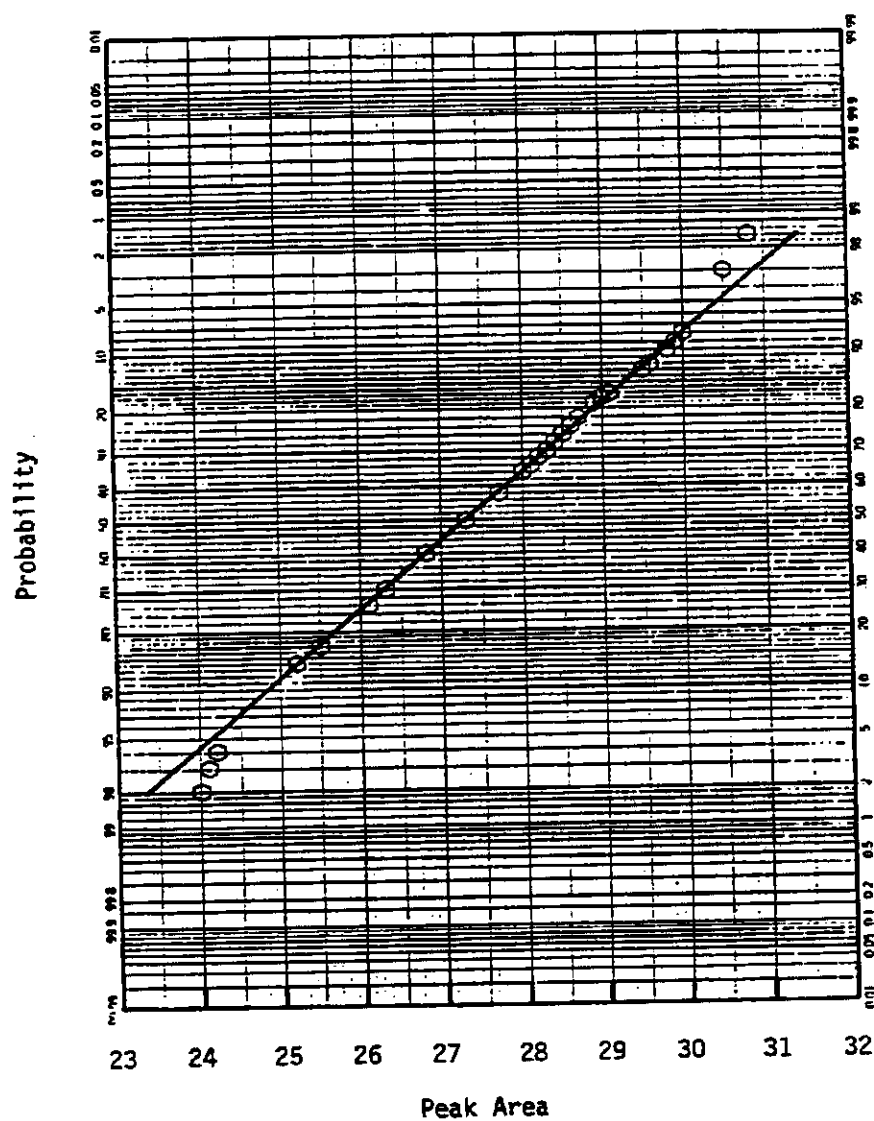


Figure N.4. Experimental Error Distribution of GC Analysis
in Terms of Measured CO_2 Peak Area.

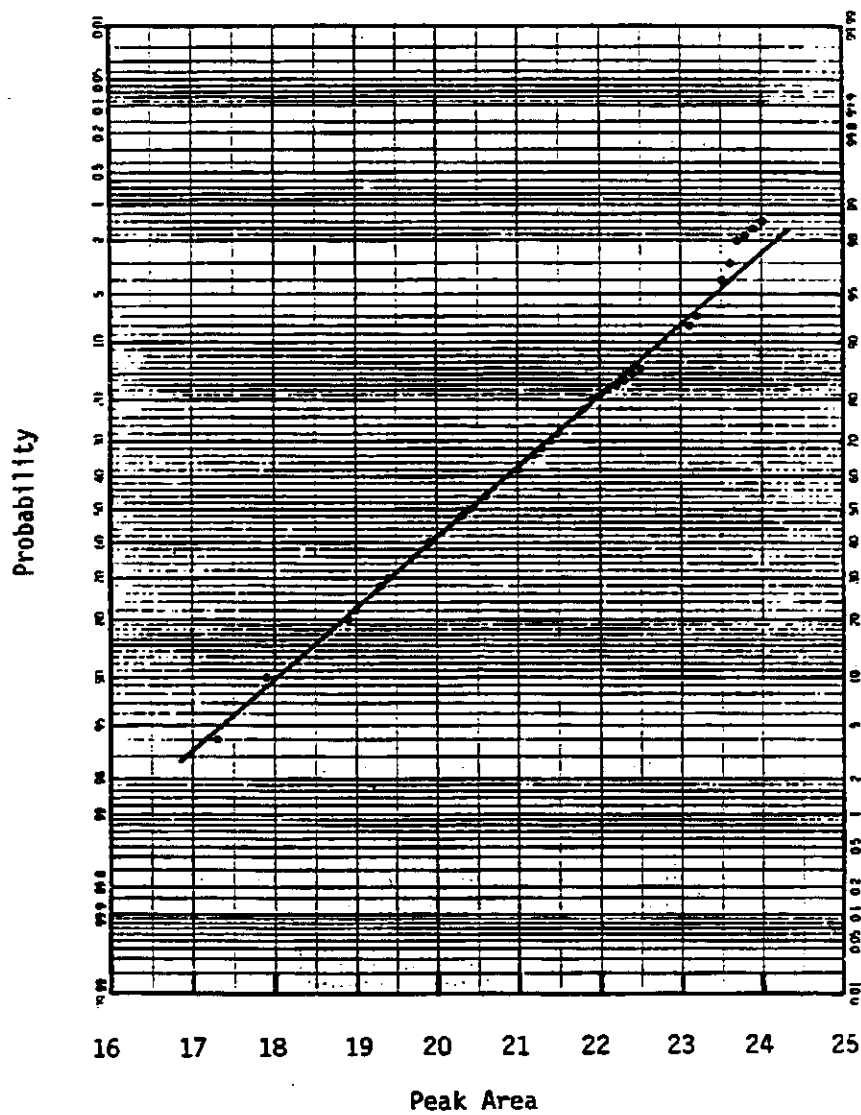


Figure N.5. Experimental Error Distribution of GC Analysis
in Terms of Measured CH_4 Peak Area.

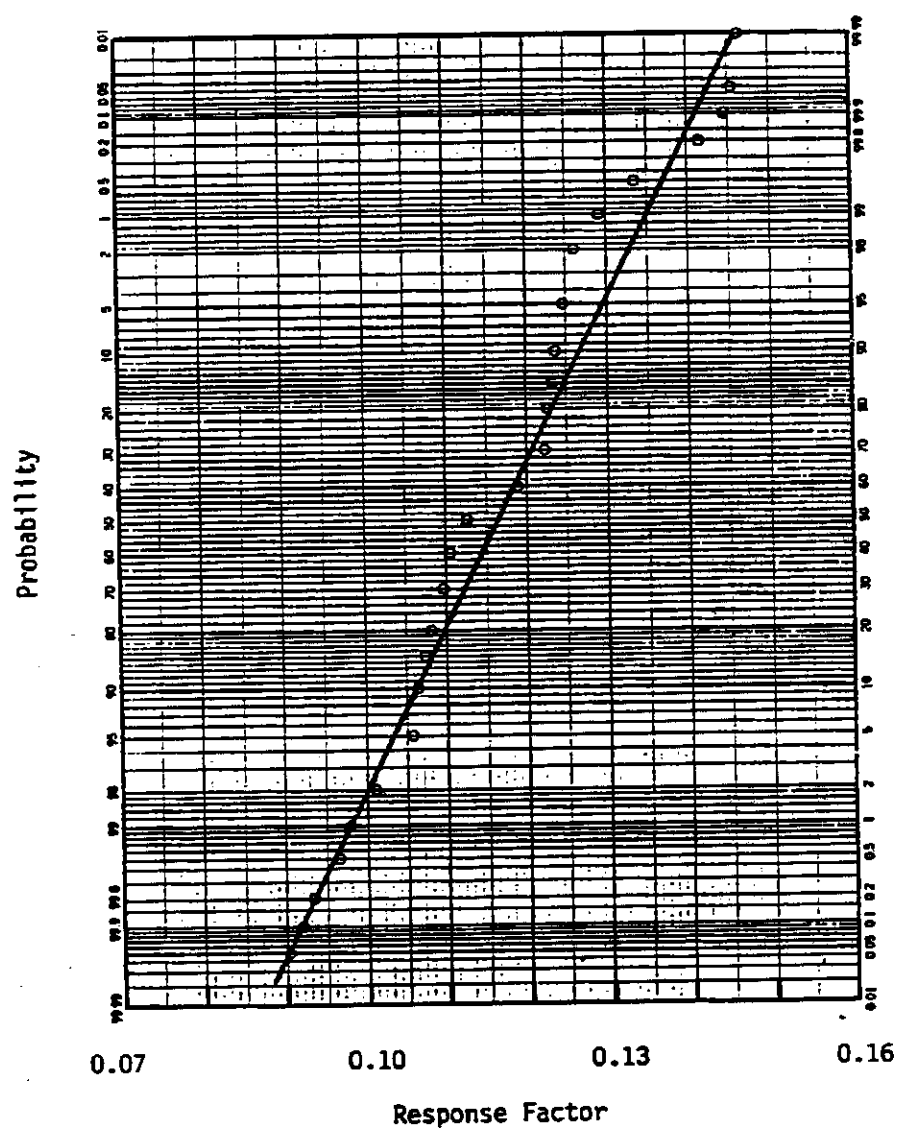


Figure N.6. Experimental Error Distribution of GC Analysis in Terms of Calculated H_2 Response Factor.

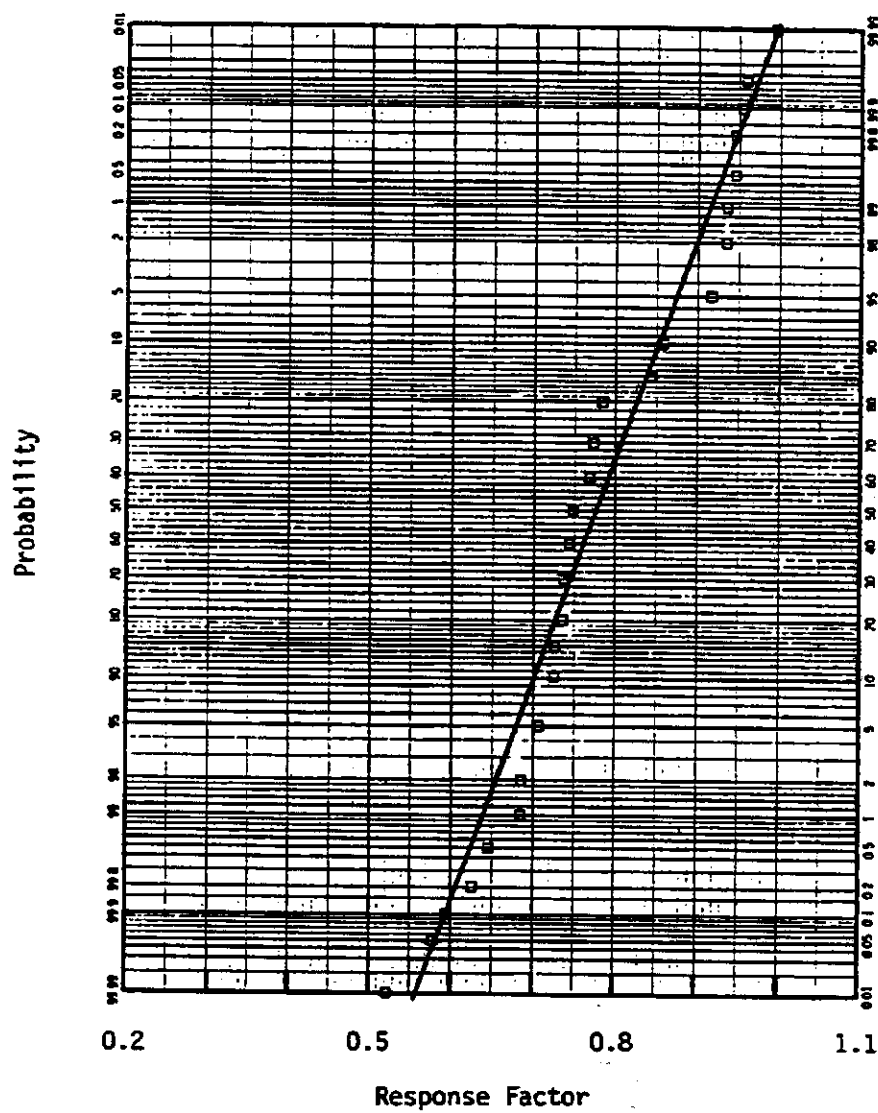


Figure N.7. Experimental Error Distribution of GC Analysis
in Terms of Calculated CO Response Factor.

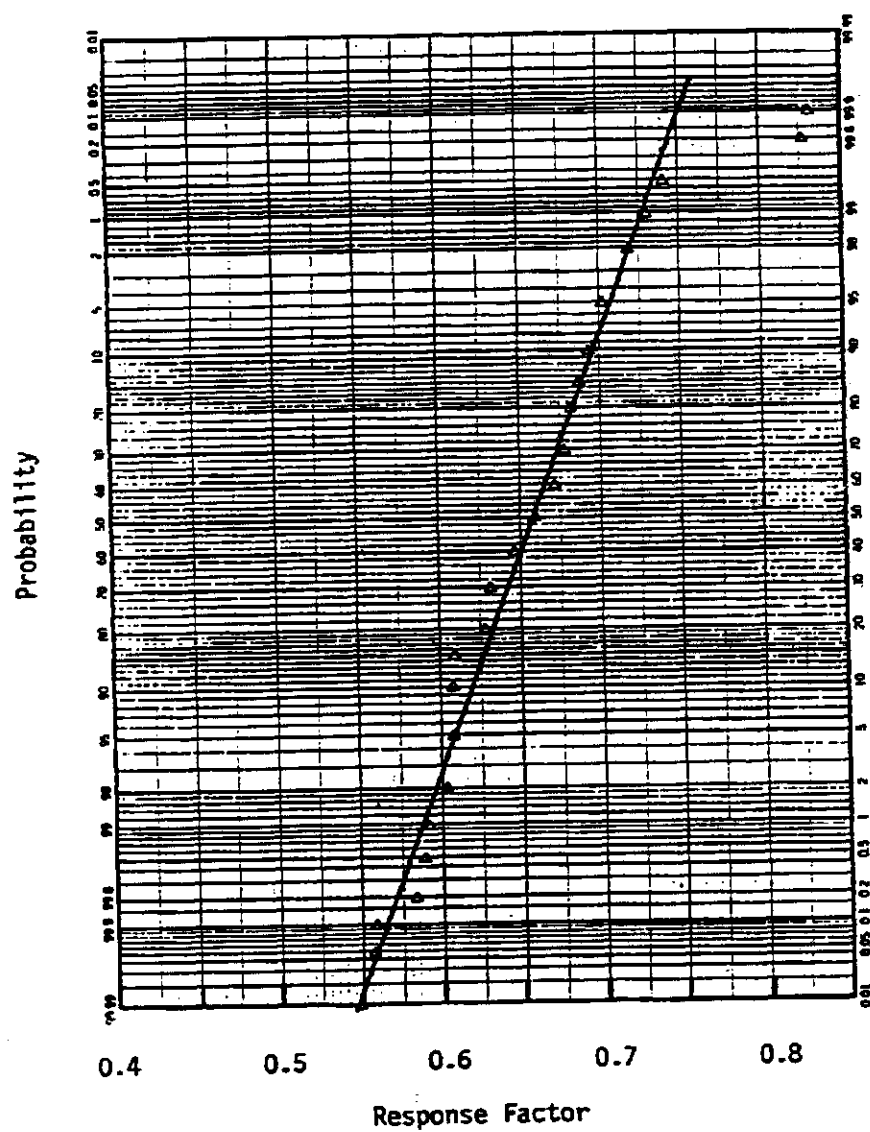


Figure N.8. Experimental Error Distribution of GC Analysis
in Terms of Calculated C_2H_4 Response Factor.

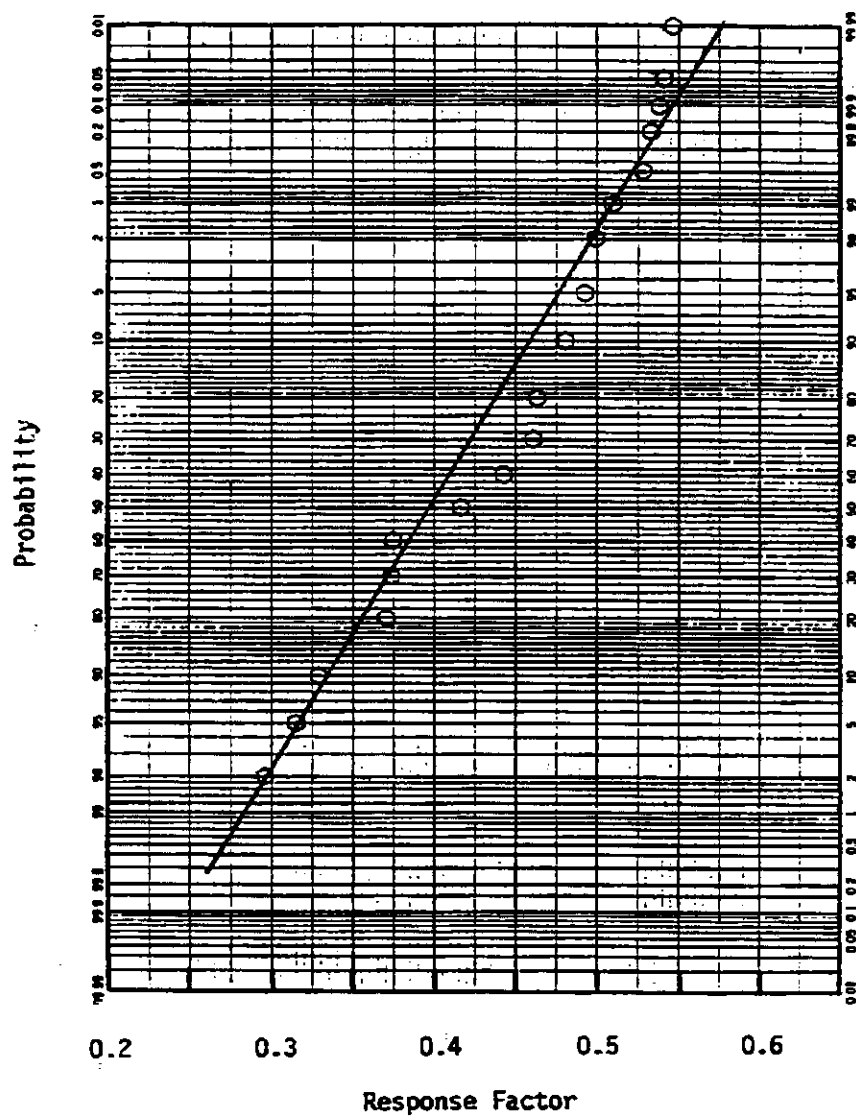


Figure N.9. Experimental Error Distribution of GC Analysis
in Terms of Calculated CH_4 Response Factor.