THEORETICAL ERRORS IN MULTICOMPONENT SPECTOPHOTOMETRIC ANALYSIS BY THE METHOD OF LEAST SQUARES.

If the extinction coefficients of the j^{th} component are $\epsilon_{1j} --- \epsilon_{ij} --- \epsilon_{rj}$ at wavelength $i = 1$ to r, then the concentrations $c_j\left(j = 1 \text{ to } n\right)$ in a mixture are calculated from the extinctions $E_i\left(i = 1 \text{ to } r\right)$ of the mixture with the equations

$$\left.\begin{array}{l} c_1\epsilon_{11} + c_2\epsilon_{12} ------ c_n\epsilon_{1n} = E_1' \\ c_1\epsilon_{21} + c_2\epsilon_{22} ------- c_n\epsilon_{2n} = E_2' \\ \vdots \\ c_1\epsilon_{r2} + c_2\epsilon_{r2} ------- c_n\epsilon_{rn} = E_r' \end{array}\right\} \begin{array}{l}\text{Calculated} \\ \text{Extinctions} \\ \text{of} \\ \text{Mixture}\end{array} \qquad \left.\begin{array}{l} E_1 \\ E_2 \\ \vdots \\ E_r \end{array}\right\} \begin{array}{l}\text{Experimental} \\ \text{Extinctions} \\ \text{of} \\ \text{Mixture.}\end{array}$$

and $S = \sum_{i=1}^{r}\left(E_i' - E_i\right)^2$ so that S, the divergence is a minimum.

$$\text{If} \quad \begin{bmatrix} \epsilon_{11}\epsilon_{12} --- \epsilon_{1n} \\ \epsilon_{21}\epsilon_{22} --- \epsilon_{2n} \\ \vdots \qquad\qquad \vdots \\ \epsilon_{r1}\epsilon_{r2} --- \epsilon_{rn} \end{bmatrix} = A \qquad \begin{bmatrix} E_1 \\ E_2 \\ \\ E_r \end{bmatrix} = E \quad \text{and} \quad \begin{bmatrix} c_1 \\ c_2 \\ \\ c_n \end{bmatrix} = C$$

$$\text{then} \quad C = \left(\tilde{A}, A\right)^{-1}\tilde{A}, E \quad = \begin{bmatrix} m_{11} m_{12} --- m_{1r} \\ m_{21} m_{22} --- m_{2r} \\ \vdots \\ m_{n1} m_{n2} --- m_{nr} \end{bmatrix} E$$

If σ_E is error in extinction coefficient,

then the error in $c_j, \sigma_j = \left[\sum_{i=1}^{r}\left(m_{ji}\right)^2\right]^{\frac{1}{2}} \sigma_E = \mathbf{P}_j\,\sigma_E$

where $\mathbf{P}_j$ is the error coefficient for the j^{th} component.