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

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

$$\left. \begin{array}{l} c_1 \epsilon_{11} + c_2 \epsilon_{12} \dots \dots \dots c_n \epsilon_{1n} = E_1 \\ c_1 \epsilon_{21} + c_2 \epsilon_{22} \dots \dots \dots c_n \epsilon_{2n} = E_2 \\ \vdots \\ c_1 \epsilon_{r1} + c_2 \epsilon_{r2} \dots \dots \dots c_n \epsilon_{rn} = E_r \end{array} \right\} \begin{array}{l} \text{Calculated} \\ \text{Extinctions} \\ \text{of} \\ \text{Mixture} \end{array} \quad \left. \begin{array}{l} E_1 \\ E_2 \\ \vdots \\ E_r \end{array} \right\} \begin{array}{l} \text{Experimental} \\ \text{Extinctions} \\ \text{of} \\ \text{Mixture.} \end{array}$$

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

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

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

If σ_E is error in extinction coefficient,

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

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