Beer's Law

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The Beer-Lambert relationship (or Beer's law) states that the concentration *C* is directly proportional to the absorbance *A*. Generally, this relationship is more often applied by comparing the height of a maximum absorption peak of a reference gas to the height of the corresponding peak in a sample spectrum. However, this technique suffers if the baseline is not accurately known, and it fails completely in those cases where an individual spectral feature of a sample is below the noise level. These problems can be reduced if the proper least square fitting routines are applied to the data.

The application of any least square method to multi-component quantitative infrared analysis requires a known relationship. Beer's law provides this required relationship. That is,

$$A = abC$$

where *a* is the absorptivity and *b* is the pathlength.

Multivariate calibration methods have had a major impact on the quantitative analysis of infrared spectral data. They have been shown to improve analysis precision, accuracy, reliability, and applicability for infrared spectral analyses relative to the more conventional univariate methods of data analysis. Rather than attemping to find and use only an isolated spectral feature in the analysis of spectral data, multivariate methods derive their power from the simultaneous use of multiple intensities (i.e. multiple variables) in each spectrum. Thus, the problem of spectral interferences can be eliminated with the use of any one of the various multivariate methods. These methods include classical least squares[i] (CLS, also known as the K-matrix method), inverse least square [ii](ILS, also known as the P-matrix method), the Q-matrix method[iii], cross correlation[iv], Kalman filtering[v], partial least square (PLS)[vi], and principal component regression [vi](PCR). The more heavily used multivariable calibration methods in infrared spectroscopy are CLS, ILS, PLS and PCR; according to Reference [vii] CLS, PLS and PCR almost always outperform the frequency limited ILS method. This is because the full-spectrum methods take advantage of the signal averaging effect obtained when multiple intensities with redundant information are included in the analysis. The standard CLS method performs almost as good as the other methods[vii]. By recommendation of Haaland[viii], a variation of the CLS method is believed to outperform PLS and PCR and used by the SPGAS software. This method is a multi-band, multi-component weighted analysis version of the CLS and is based on the work of Haaland *et al* [ix,x and xi].

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