EXAMINATION CRITERIA AND UNCERTAINTY OF TRACE LEVELS OF ORGANIC COMPOUNDS IN COMPLEX MATRICES BY GC-MS

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The identification of trace levels of compounds in complex matrices by conventional low-resolution gas chromatography hyphenated with mass spectrometry is based in the comparison of retention times and abundance ratios of characteristic mass spectrum fragments of analyte peaks from calibrators with sample peaks. Statistically sound criteria for the comparison of these parameters were developed based in the normal distribution of retention times and in the simulation of possible non-normal distribution of correlated abundances ratios (Figure). The confidence level used to set the statistical maximum and minimum limits of parameters define the true positive rates of identifications. The false positive rate of identification were estimated from worst-case signal noise models. The estimated true and false positive rate of identifications from one retention time and two correlated ratios of three fragments abundances were combined using simple Bayes statistics to estimate the probability of compound identification being correct designated examination uncertainty. Models of the variation of examination uncertainty with analyte quantity allowed the estimation of the Limit of Examination as the lowest quantity that produce "Extremely strong" evidences of compound presence. User friendly MS-Excel files are made available to allow the easy application of developed approach in routine and research laboratories. The developed approach was successfully applied to the identification of chlorpyrifos-methyl and malathion in QuEChERS method extracts of vegetables with high water content for which the estimated Limit of Examination is 0.14 mg kg^{-1} and 0.23 mg kg^{-1} respectively.

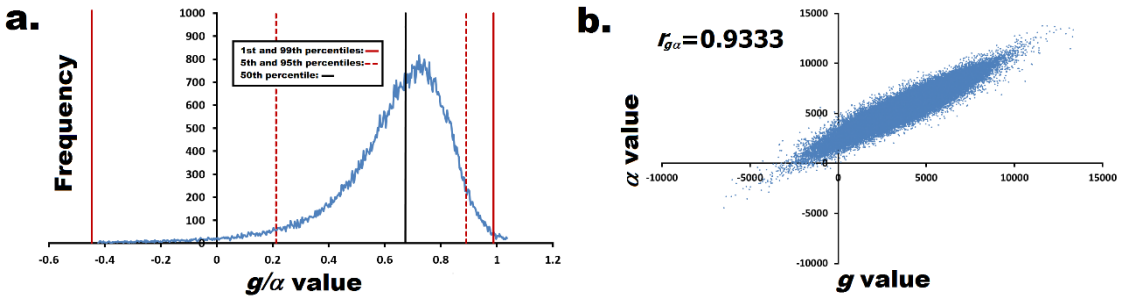

Figure: a – Distribution of simulated abundance ratios of fragments 117 m/z, *g*, and 127 m/z, *α*, in the identification of 0.25 mg L^{-1} malathion in solvent. The distribution of the ratio is asymmetric. b – Correlation of simulated *g* and *α* values (Pearson's correlation coefficient of 0.9333).

[1] R. J. N. Bettencourt da Silva, *Evaluation of trace analyte identification in complex matrices by low-resolution gas chromatography - mass spectrometry through signal simulation*, Talanta 150 (2016) 553-567.