ELECTROSPRAY IONIZATION MATRIX EFFECT AS AN UNCERTAINTY SOURCE IN HPLC/ESI-MS PESTICIDE RESIDUE ANALYSES

Anneli Kruve[1] (presenting author), Koit Herodes[1], Ivo Leito[1]
[1] Institute of Chemistry, University of Tartu, Estonia
e-mail: anneli.kruve@ut.ee

LC/ESI/MS is frequently used to analyze different compounds from pharmaceuticals to pesticides. Even though MS^2 can be applied to confirm the identity of the compound ionization suppression/enhancement, called matrix effect, of the analyte may occur in the ion source (ESI) due to co-eluting compounds.

The matrix effects in LC/ESI/MS analysis are difficult to compensate for due to their large variability. Therefore matrix effect could be taken into account through uncertainty. An empirical approach – *matrix effect graph* approach – for estimating the uncertainty due to matrix effect in LC/ESI/MS analysis of pesticide residues in fruits and vegetables has been adapted.

For this approach calibration graphs, evaluated after every one month, using extracts of different fruits/vegetables as calibration solutions, are prepared and a regression line is fitted through these data. These fruits/vegetables may be either from the commodity group of the samples or from different commodity groups. The relative residuals of the calibration points peak areas are calculated and plotted against the measurement time. We term the resulting graph as the *matrix effect graph*. The root mean square of the relative residuals is calculated and used as the estimate of relative uncertainty of the sample peak areas caused by the matrix effect. *Matrix effect graph* obtained over fruits/vegetables from different commodity groups can also be used for identifying fruits/vegetables with extreme matrix effects.
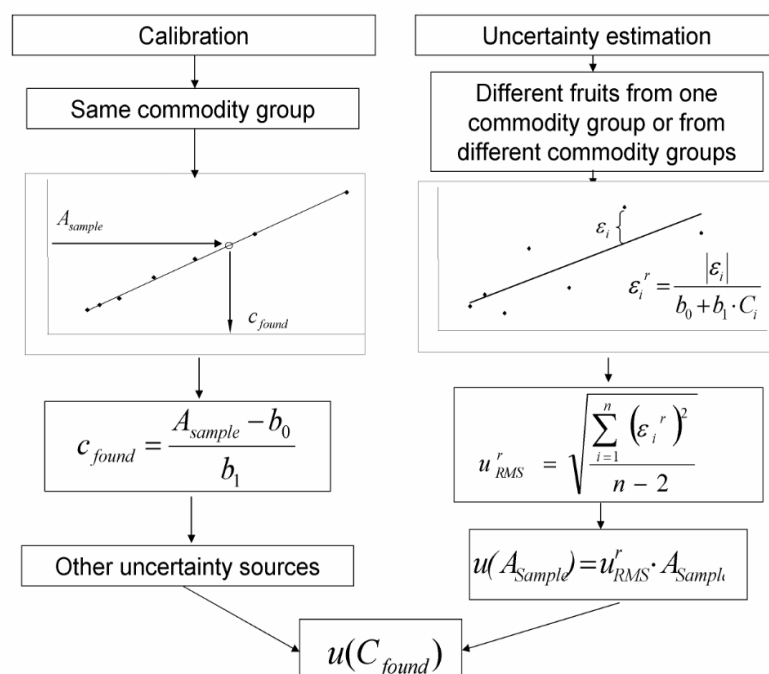

Figure 1 Workflow for the calculation of c_{found}, u^r_{RMS}, and $u_c(c_{found})$.

The *matrix effect graph* approach was used for determination of thiabendazole, aldicarb, imazalil and methiocarb and was validated with tomato, cucumber and sweet corn matrixes at 0.5 mg/kg concentration level. When different commodity groups were used for compiling the matrix effect graph then results of analysis of all samples agree with the spiked concentrations within the expanded uncertainties (at $k = 2$ level). When the matrix effect graph was compiled using fruits from the same commodity group as the analyzed samples (fruiting vegetables in this case) then agreement was found in 98% of cases.

References:
1. A. Kruve, K. Herodes, I- Leito, *J AOAC Int,* **93**, (2010) 9