SUPPLEMENTARY MATERIALS

Estimation of the limit of detection in chromatography from calibration data: limitations of ordinary least squares regression and advantages of using weighted least squares

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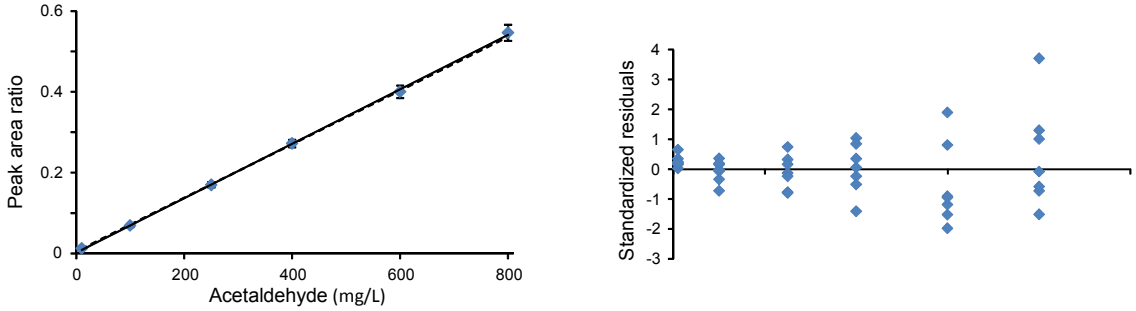
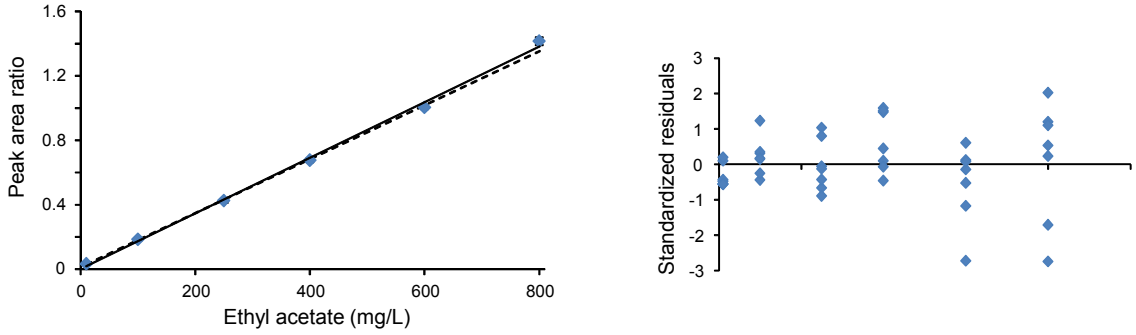
Methods evaluated

Brief description of the methods evaluated in the study, with the calibration graph (left side) and standardized residuals distribution plot (calculated by OLS, right side) obtained for each method. The continuous line in the calibration graph corresponds to the regression line calculated by OLS, whereas the dashed line corresponds to the WLS regression using $1/s_i^2$ as the weighting factor.

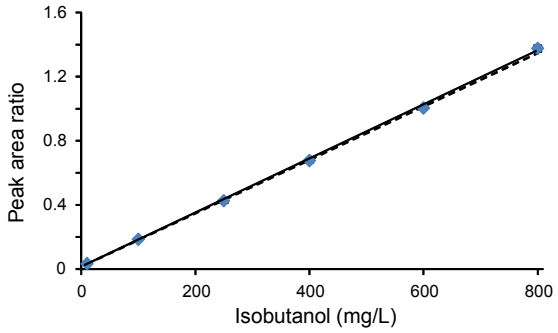
GC-FID #1: Determination of acetaldehyde in hydro-alcoholic matrix by direct injection using internal standard (IS) quantification; working range: 10-800 mg/L

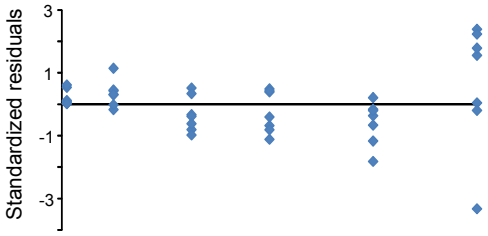


GC-FID #2: Determination of ethyl acetate in hydro-alcoholic matrix by direct injection using IS; working range: 10-800 mg/L

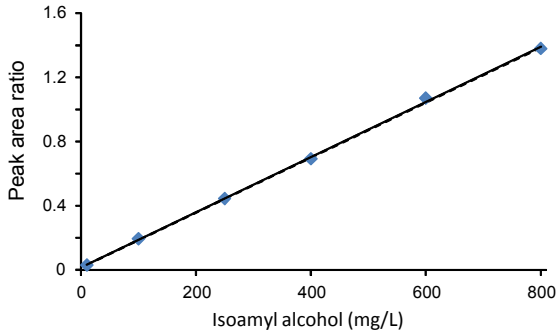


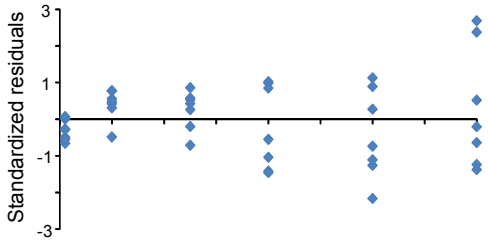
GC-FID #3: Determination of isobutanol in hydro-alcoholic matrix by direct injection using IS; working range: 10-800 mg/L



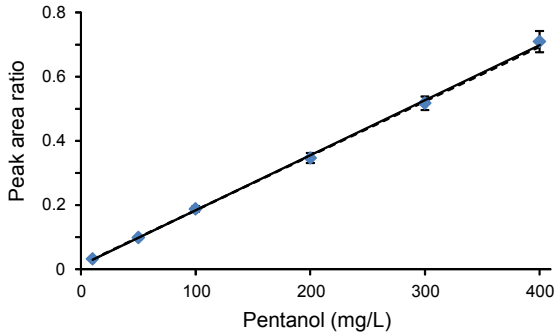


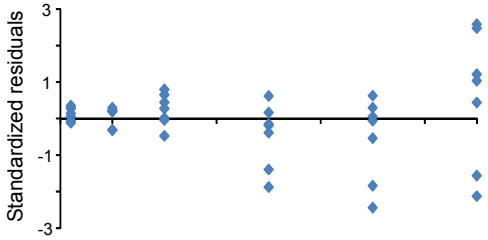
GC-FID #4: Determination of isoamyl alcohol in hydro-alcoholic matrix by direct injection using IS; working range: 10-800 mg/L



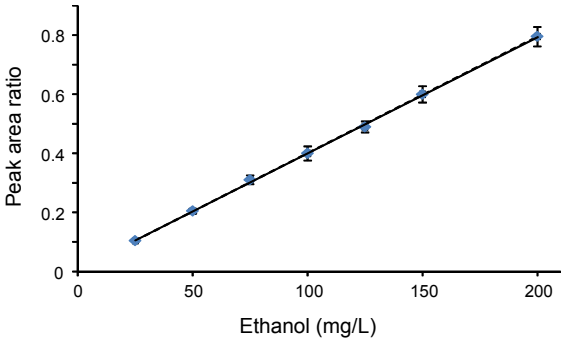


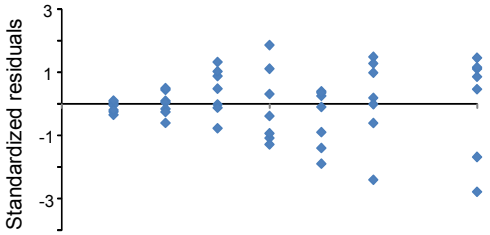
GC-FID #5: Determination of pentanol in hydro-alcoholic matrix by direct injection using IS; working range: 10-400 mg/L



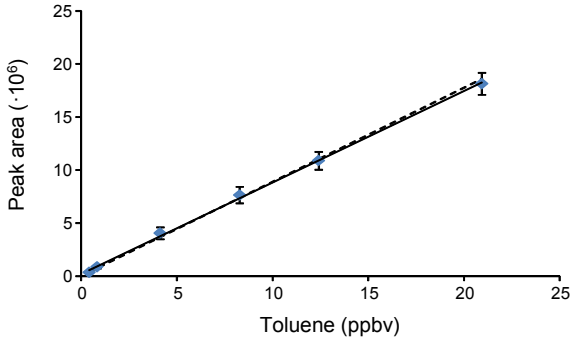


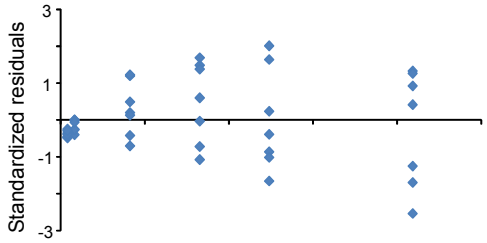
GC-FID #6: Determination of ethanol in urine by head-space using IS; working range: 25-200 mg/L


Peak area ratio
0.8
0.6
0.4
0.2
0
0
50
100
150
200
Ethanol (mg/L)

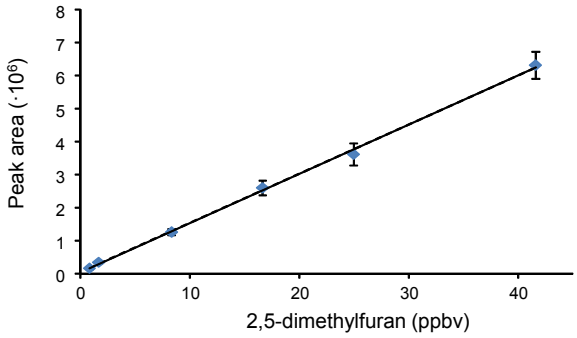

Standardized residuals
3
1
-1
-3

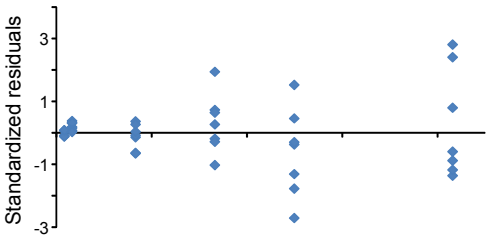
GC-MS #1: Determination of toluene in breath samples (active sampling and thermal desorption); working range: 0.4-21 ppbv



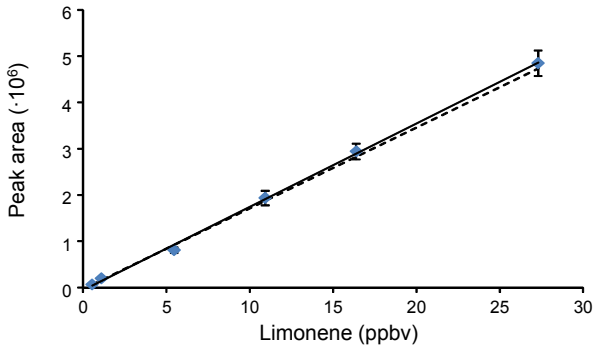


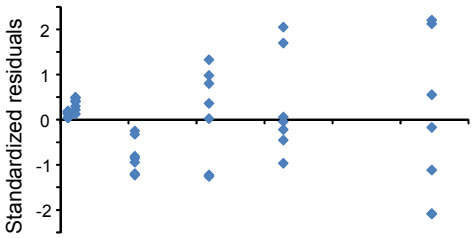
GC-MS #2: Determination of 2,5-dimethylfuran in breath samples (active sampling and thermal desorption); working range: 0.8-42 ppbv



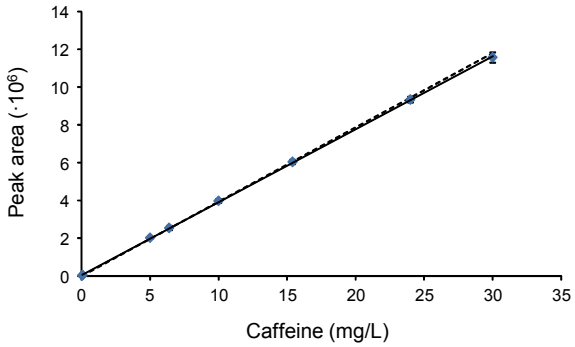


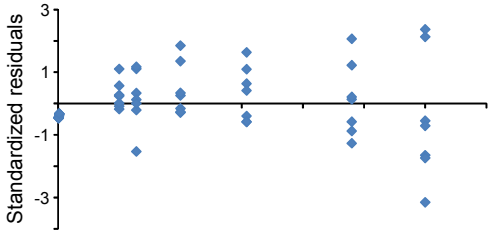
GC-MS #3: Determination of limonene in breath samples (active sampling and thermal desorption); working range: 0.6-28 ppbv



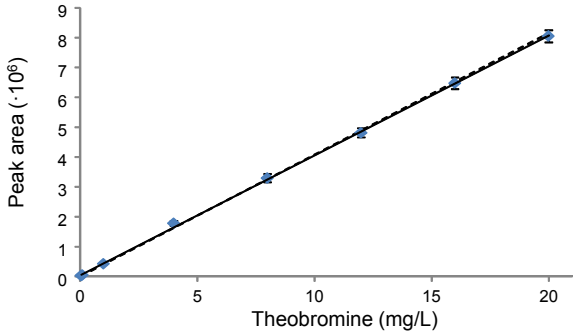


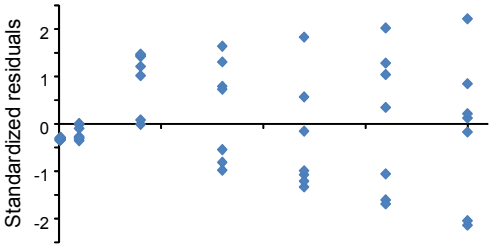
HPLC-UV #1: Determination of caffeine in beverages; working range: 0.1-30 mg·L^{-1}



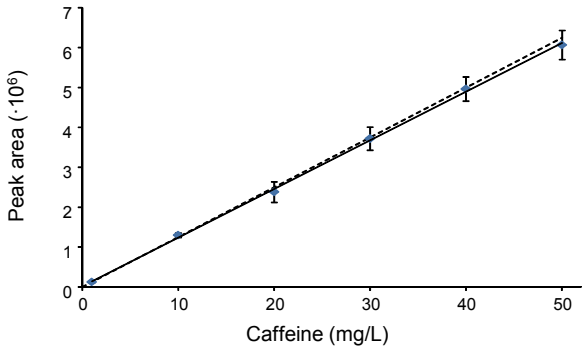


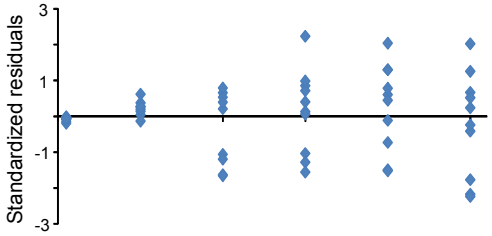
HPLC-UV #2: Determination of theobromine in tea samples; working range: 0.1-20 mg·L^{-1}



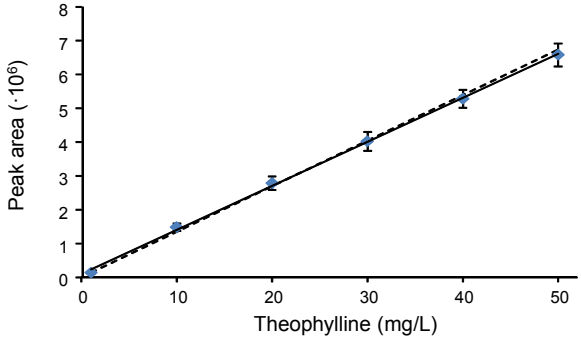


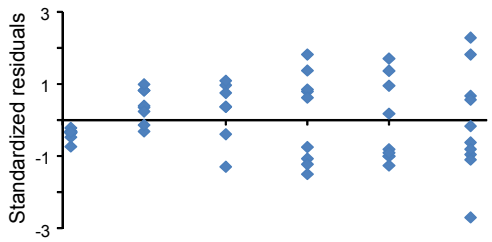
HPLC-UV #3: Determination of caffeine in coffees; working range: 1-50 mg·L^{-1}



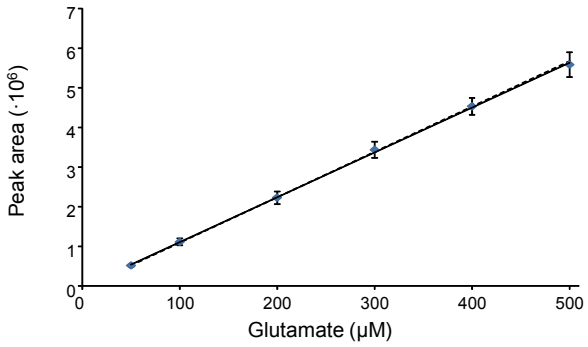


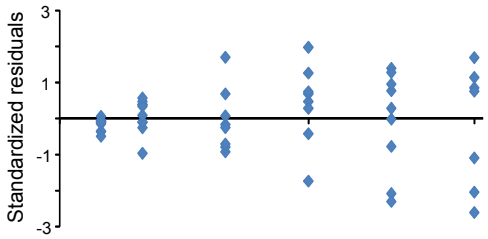
HPLC-UV #4: Determination of theophylline in teas; working range: 1-50 mg·L^{-1}



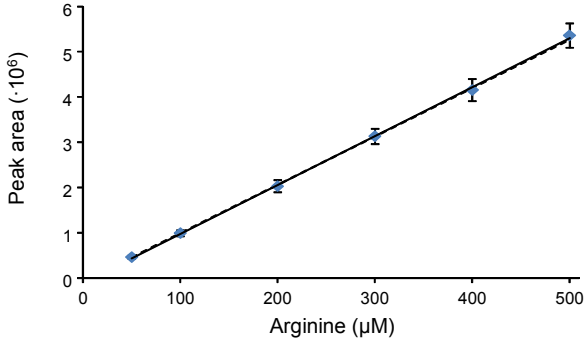


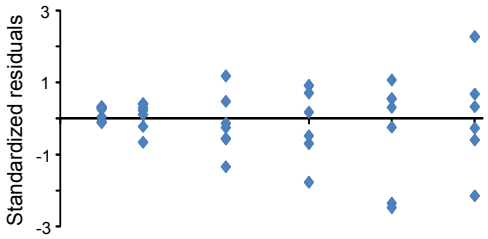
HPLC-UV #5: Determination of glutamate in plasma samples (off-line derivatization with AQC); working range: 50-500 µM



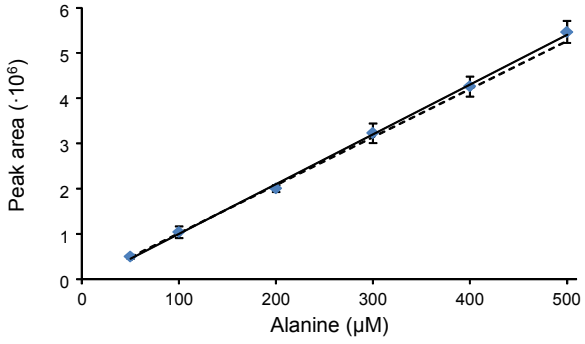


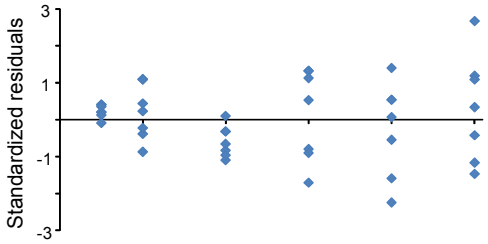
HPLC-UV #6: Determination of arginine in plasma samples (off-line derivatization with AQC); working range: 50-500 µM



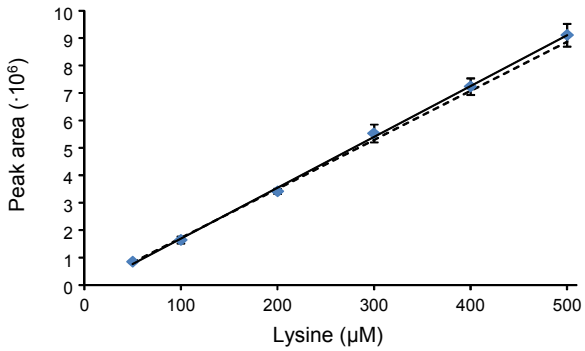


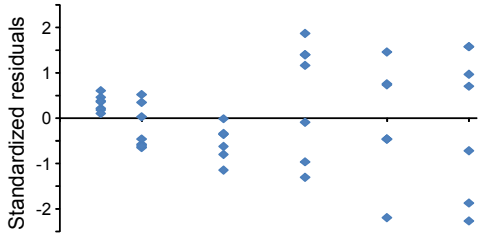
HPLC-UV #7: Determination of alanine in plasma samples (off-line derivatization with AQC); working range: 50-500 µM



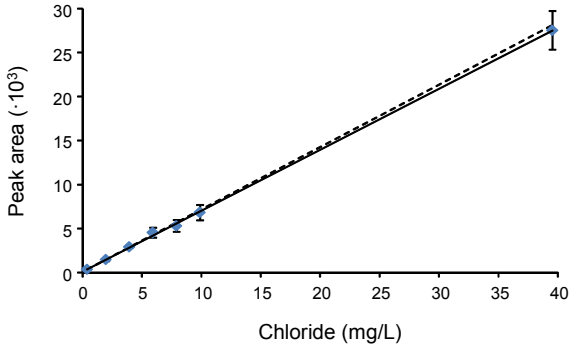


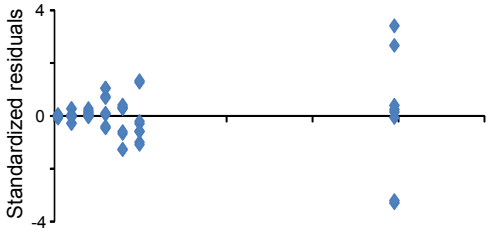
HPLC-UV #8: Determination of lysine in plasma samples (off-line derivatization with AQC); working range: 50-500 µM



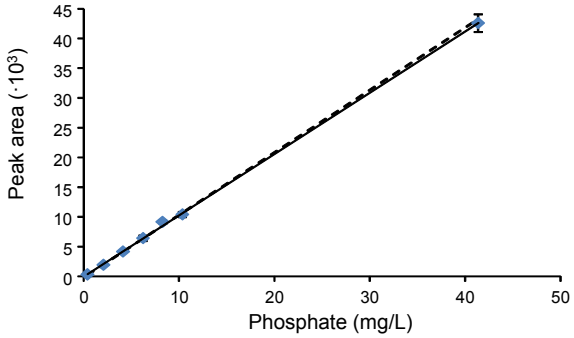


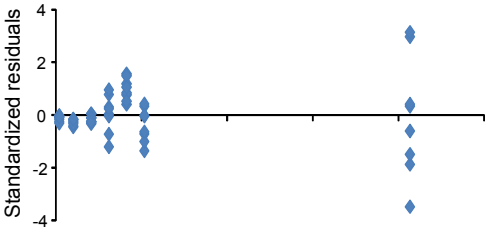
CZE-UV #1: Determination of chloride in natural waters; working range: 0.4-40 mg·L^{-1}



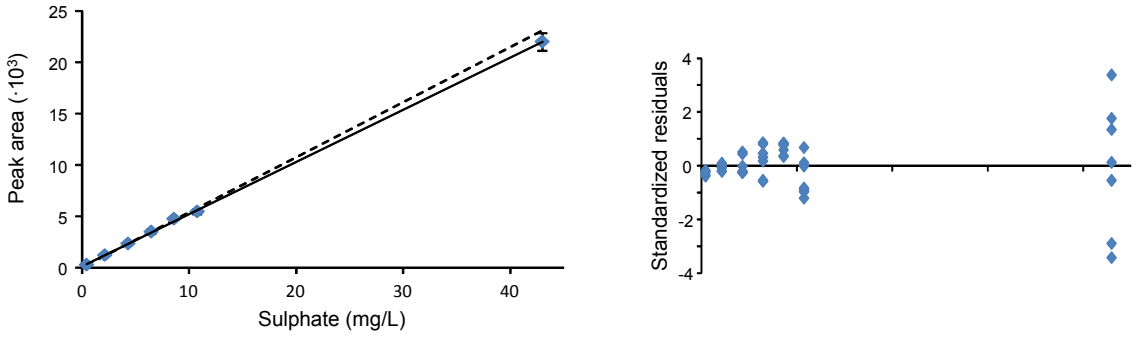


CZE-UV #2: Determination of phosphate in natural waters; working range: 0.4-42 mg·L^{-1}





CZE-UV #3: Determination of sulphate in natural waters; working range: 0.4-43 mg·L^{-1}



Calibrations rejected

Two calibration curves were rejected because they were not considered linear. Figure S1 shows the results obtained for one of the HPLC-UV methods rejected. Despite the lack-of-fit (LOF) test gave *p*=0.260, suggesting linearity, the Mandel's test yielded F=377.7, above the tabulated values of 10.13 (α=0.05,1,3) and 34.12 (α=0.01,1,3). The result of the Mandel's test indicates that the variance explained by the addition of a quadratic factor to the linear model was statistically significant and does not only correspond to random errors.

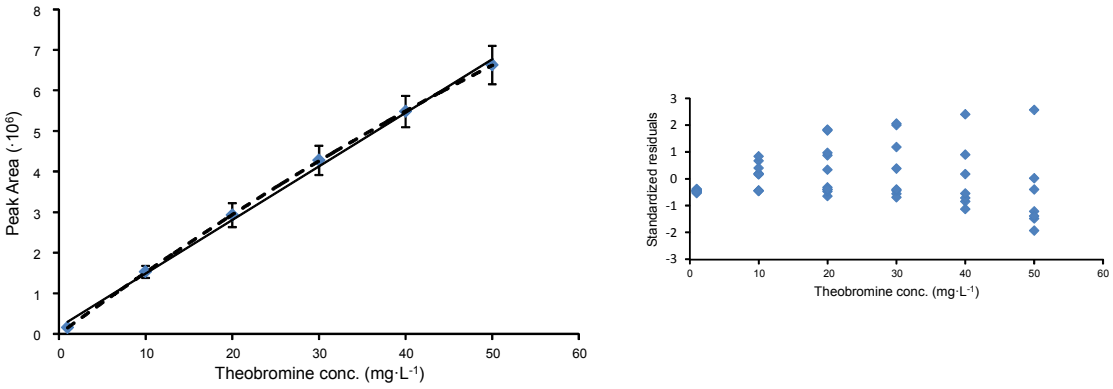


Figure S1. Calibration curves and residual plot obtained for an HPLC-UV method for the analysis of theobromine in chocolate samples. Each calibration point is the mean of seven replicate standards and the error bars show the standard deviations obtained at each level. Solid line shows the linear trend obtained applying ordinary least squares (y = 132044 x + 174473; R^2 = 0.997305). Dashed line corresponds to the quadratic polynomial fitting (y = -483 x^2 + 156606 x – 1177; R^2_{cor} = 0.999965).