Supplementary Information (SI)

Fast, Cheap and Easy routine quantification method for atrazine and its transformation products in water matrixes using DLLME-GC/MS method

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Analysis of Variance (ANOVA) for ATZ. DEA and DIA extractions

Table S1. Analysis of variance (ANOVA) for extraction of ATZ by DLLME using quadratic model Doehlert matrix.

Source of Variation	**SS**	**df**	**MS**	**Fcal**		**ρ**
Regression	17.97	9	2.00	13.82	**SG**	0.0003
Residual	1.30	9	0.14			
Lack-of-fit	0.41	3	0.13	0.90		0.4950
Pure Error	0.90	6	0.15			
Total SS	19.27	18				
% Explained Variation				93.25		
% Maximum Explained Variation				95.34		

Where: SS: Sums of Squares; df: Degree of Freedom; MS: Mean Square; Fcalc: calculated F value; ρ: significance level; SG: Significant.

Table S2. Analysis of variance (ANOVA) for extraction of DEA by DLLME using quadratic model Doehlert matrix.

Source of Variation	**SS**	**df**	**MS**	**Fcal**		**ρ**
Regression	234.00	9	26.00	21.29	**SG**	0.00005
Residual	11.00	9	1.22			
Lack-of-fit	3.53	3	1.18	0.95		0.475
Pure Error	7.46	6	1.24			
Total SS	245.00	18				
% Explained Variation				95.51		
% Maximum Explained Variation				96.96		

Where: SS: Sums of Squares; df: Degree of Freedom; MS: Mean Square; Fcalc: calculated F value; ρ: significance level; SG: Significant.

Table S3. Analysis of variance (ANOVA) for extraction of DIA by DLLME using quadratic model Doehlert matrix.

Source of Variation	SS	df	MS	Fcal		ρ
Regression	55.73	9	6.19	24.80	**SG**	0.00003
Residual	2.25	9	0.25			
Lack-of-fit	0.83	3	0.28	1.18		0.3921
Pure Error	1.41	6	0.24			
Total SS	57.98	18				
% Explained Variation				96.12		
% Maximum Explained Variation				97.56		

Where: SS: Sums of Squares; df: Degree of Freedom; MS: Mean Square; Fcalc: calculated F value; ρ: significance level; SG: Significant.

Normal probability graphs of the effects of each variable

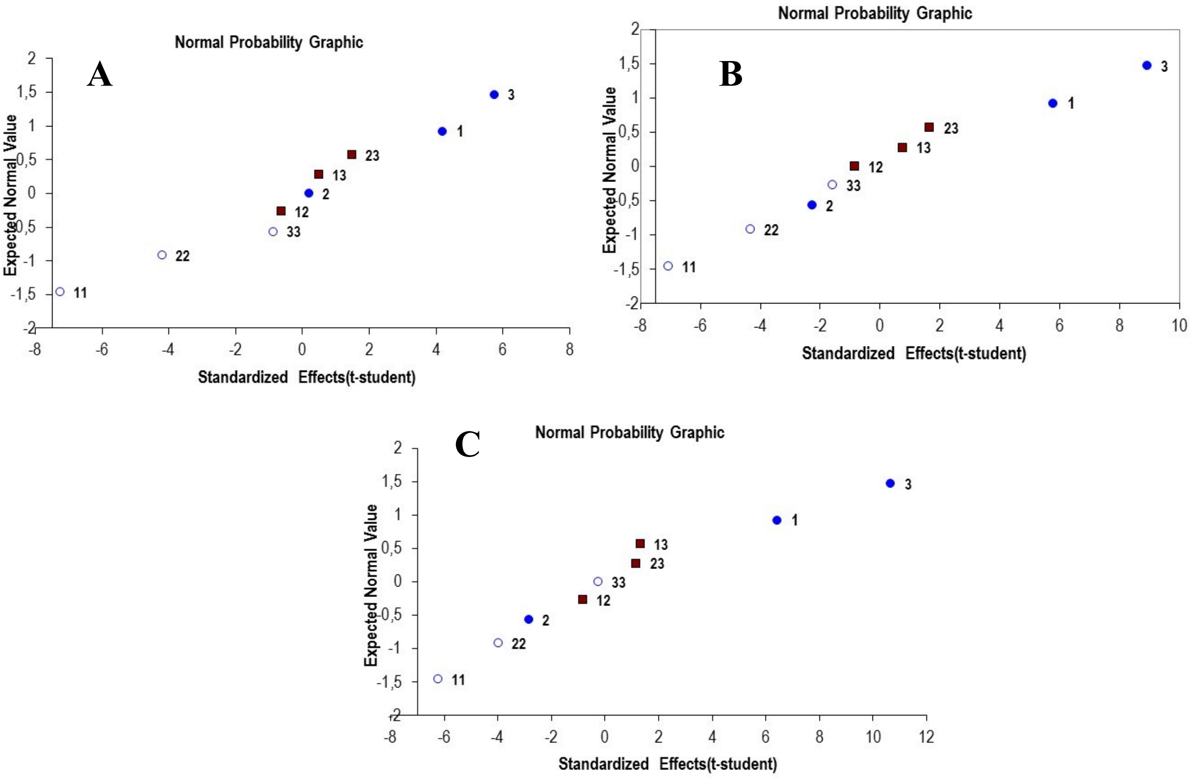

Figure S1. Normal probability graphs of the effects of each variable - 1) Extraction Solvent; 2) Dispersive Solvent and 3) ionic strength. For: (A) ATZ; (B) DEA and (C) DIA.

Surface Response Study

The quadratic model was used to plot the response surface graphs represented by equations 1S and 2S. 3S and 4S. 5S and 6S for ATZ. DEA and DIA respectively. The equations 1S. 3S and 5S represent the interactions between the ionic strength and the DS. interactions of ionic strength and ES are represented by equations 2S. 4S and 6S.

$$Y=-1.27X_1^2-0.25X_2^2+0.74X_1X_2+0.04X_1+1.09X_2 +5.60 \quad (1S)$$

$$Y=-2.21X_1^2-0.25X_2^2-0.25X_1X_2+0.80X_1+1.091X_2 +5.60 \quad (2S)$$

$$Y=-3.784X_1^2-1.31X_2^2+2.37X_1X_2-1.25X_1+4.92X_2 +15.03 \quad (3S)$$

$$Y=-6.26X_1^2-1.31X_2^2+1.06X_1X_2+3.20X_1+4.92X_2 +15.03 \quad (4S)$$

$$Y=-1.60X_1^2-0.09X_2^2+0.85X_1X_2-0.71X_1+2.66X_2 +15.03 \quad (5S)$$

$$Y=-2.49X_1^2-0.09X_2^2-0.76X_1X_2+1.61X_1+2.66X_2 +5.83 \quad (6S)$$

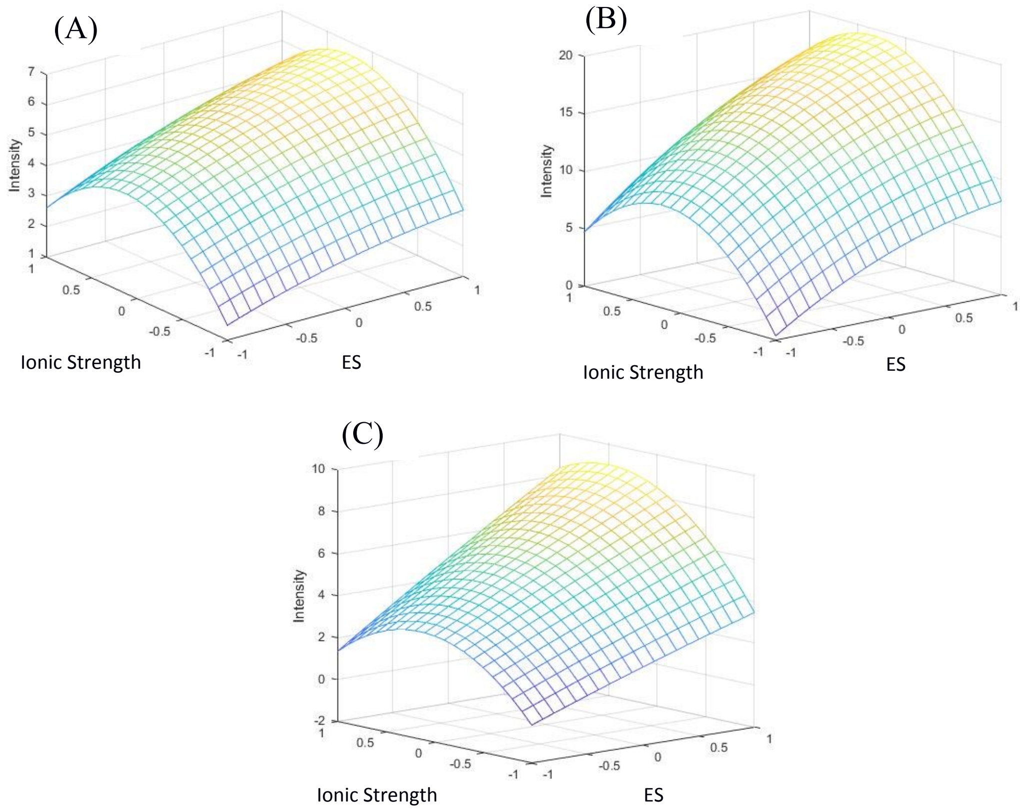

Figure S2. Representation of the response surfaces for the interaction between ionic strength and ES obtained for the Doehlert planning in the optimization of DLLME for: (A) ATZ; (B) DEA; (C) DIA.

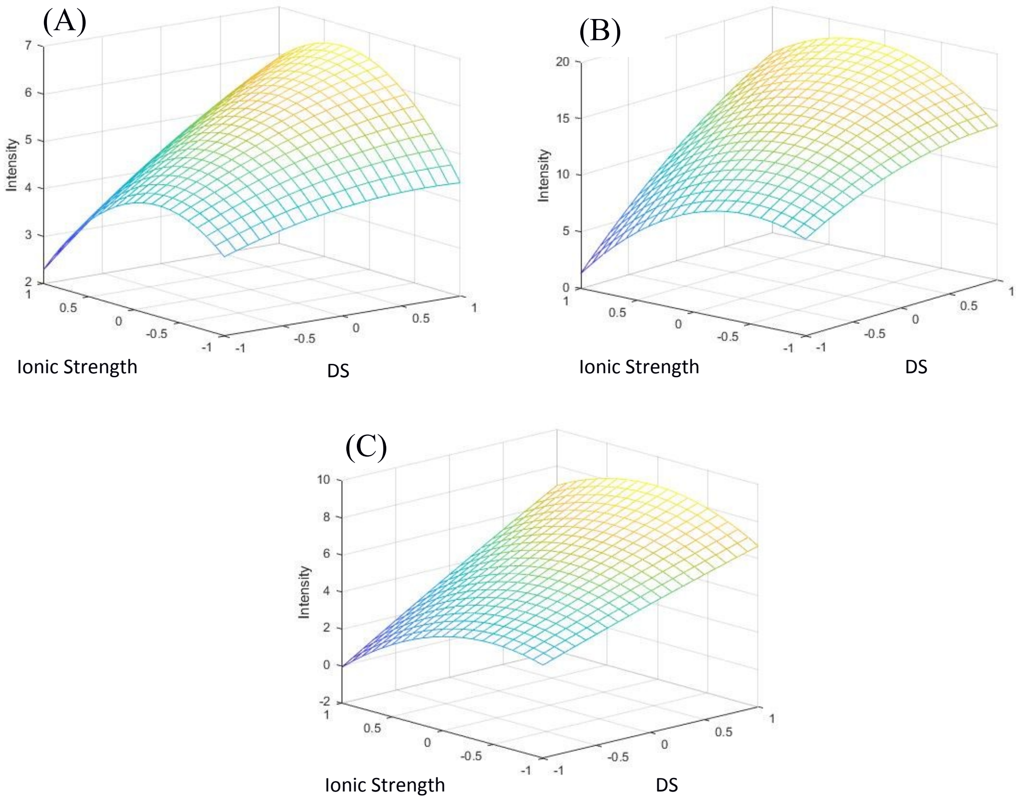

Figure S3. Representation of the response surfaces for the interaction between ionic strength and DS obtained for the Doehlert planning in the optimization of DLLME for: (A) ATZ; (B) DEA; (C) DIA.

DLLME/GC-MS method validation

Selectivity evaluation

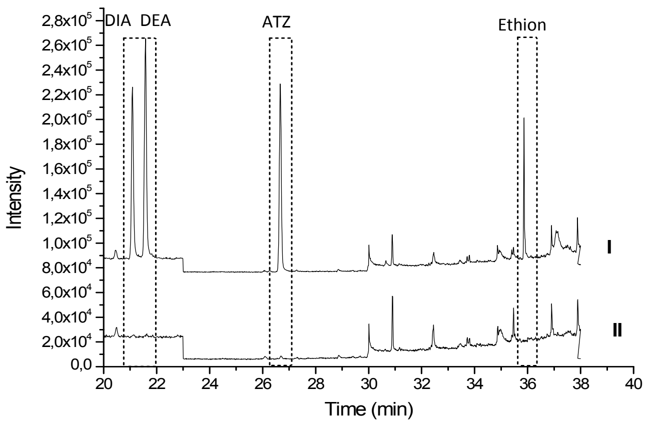

Figure S4. Chromatogram in: I) matrix fortified with ATZ, DEA (2.0µg L^{-1}) and DIA (3.0µg L^{-1}) and Ethion (2.0µg L^{-1}). II) non-fortified matrix.

Linearity evaluation

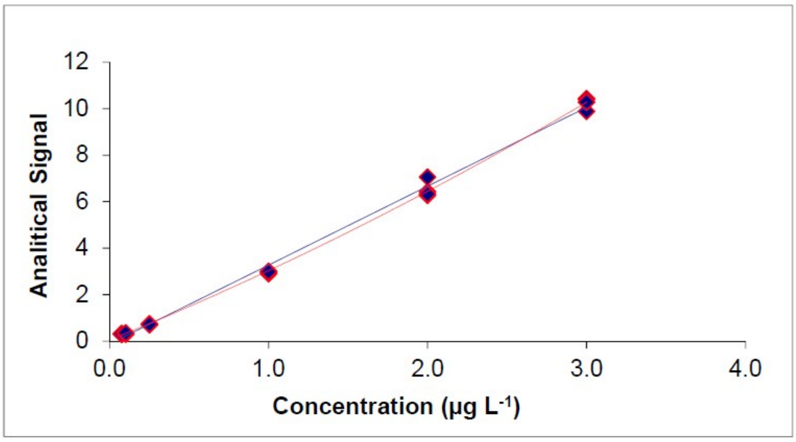

Figure S5. Curve ATZ in SWM.

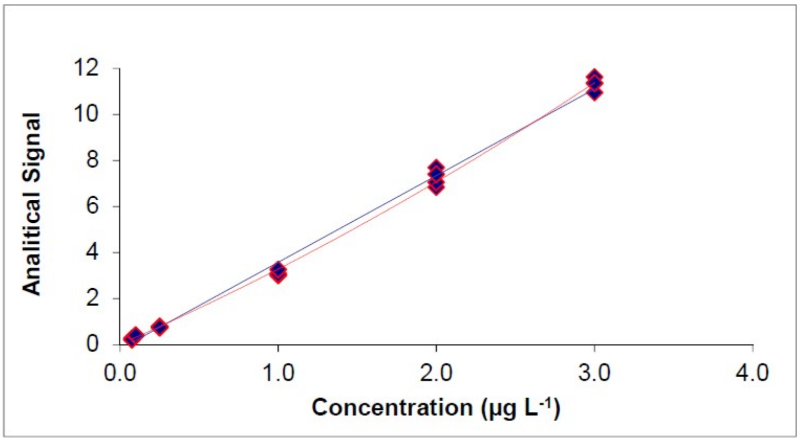

Figure S6. Curve DEA in SWM.

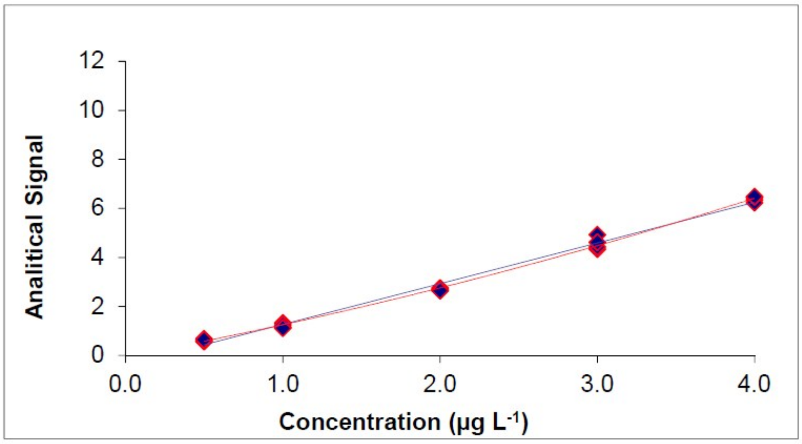

Figure S7. Curve DIA in SWM.

Residue Graphs for each of the analytical curves of ATZ, DIA and DEA

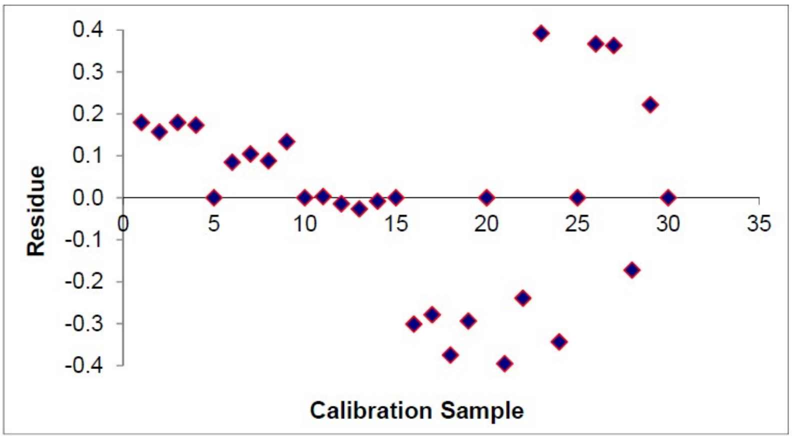

Figure S8. Residue for ATZ curve.

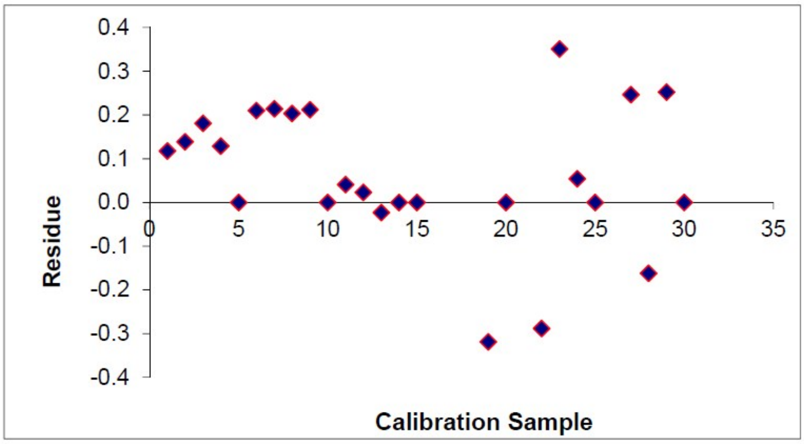

Figure S9. Residue for DEA curve.

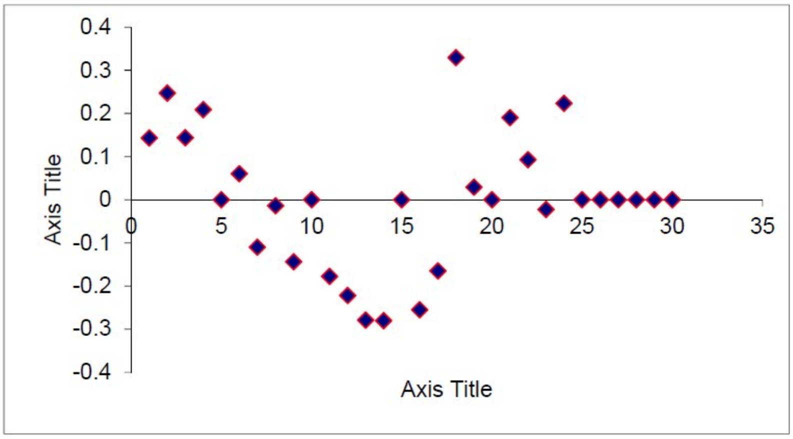

Figure S10. Residue for DIA curve.

Matrix Effect Study

Table S4. Analytical curves elaborated for the matrix effect study in UPW and SW matrix.

Analyte	Matrix	Linear range (µg L^{-1})	R^2	A	B	error	n	Matrix Effects		
								nDF	t_{calc}	t_{crit}
ATZ	UPW	0.075-3.000	0.9936	2.809	0.0587	0.0356	41	63	56.27	2.00
	SW	0.075-3.000	0.9956	3.389	-0.1098	0.04682	24			
DEA	UPW	0.25-3.000	0.9943	2.949	-0.0184	0.04022	42	64	67.40	2.00
	SW	0.25-3.000	0.9947	3.762	-0.1833	0.05743	24			
DIA	UPW	0.50-4.000	0.9918	1.330	-0.0478	0.02471	25	43	37.51	2.02
	SW	0.50-4.000	0.9917	1.663	-0.3973	0.03483	20			

Stability Study

Table S5. Stability study for ATZ. DEA and DIA in SWM from BP3.

Period	ATZ	Recovery	DEA	Recovery	DIA	Recovery

	($\mu g\ L^{-1}$)	%	($\mu g\ L^{-1}$)	%	($\mu g\ L^{-1}$)	%
Week 0	1.21 [a]	-	1.12 [a]	-	1.20 [a]	-
Week 1	1.25 [a]	103.3	1.20 [a]	108.0	1.27 [a]	105.5
Week 2	1.18 [a]	97.1	1.21 [a]	108.3	1.30 [a]	108.1
Week 3	0.97 [a]	80.3	1.04 [a]	93.4	1.25 [a]	103.5
Week 4 (Month 1)	1.11 [a]	91.2	1.04 [a]	92.8	1.13 [a]	93.9
Month 2	1.10 [a]	90.9	1.01 [a]	90.2	0.99 [a]	82.0

Analysis performed in two replicates. Equal lowercase letters in the same column indicate that no significant differences between weeks ($p < 0.5$) was verified.