Supplementary Information for Analyst

Towards on-site analysis of complex matrices by solid-phase microextraction-transmission mode coupled to a portable mass spectrometer via direct analysis in real time

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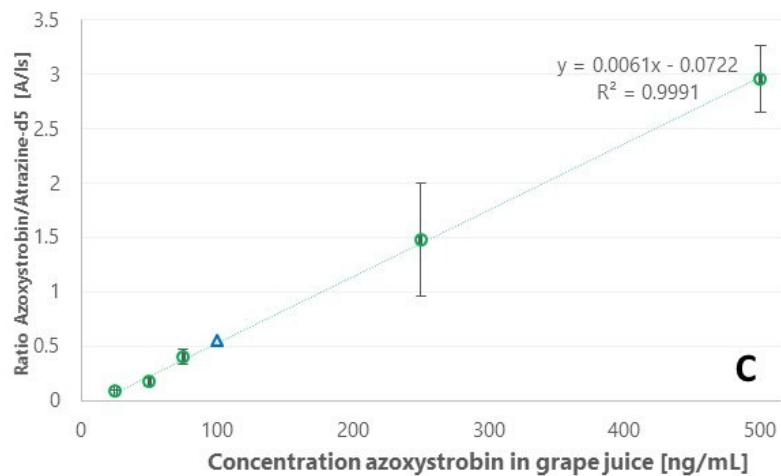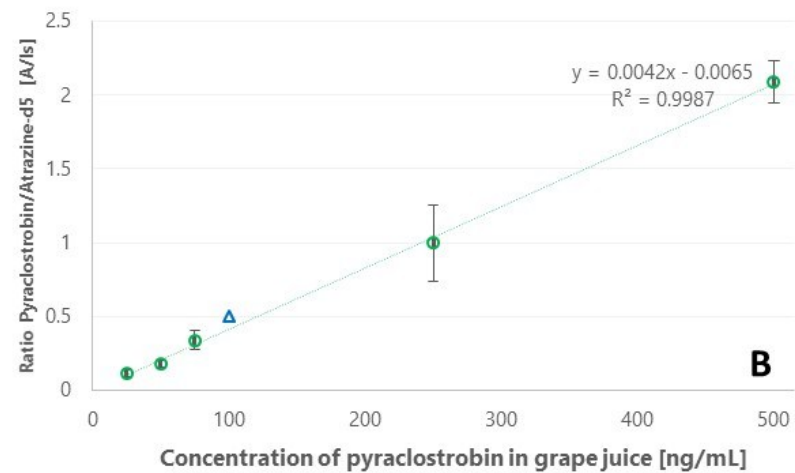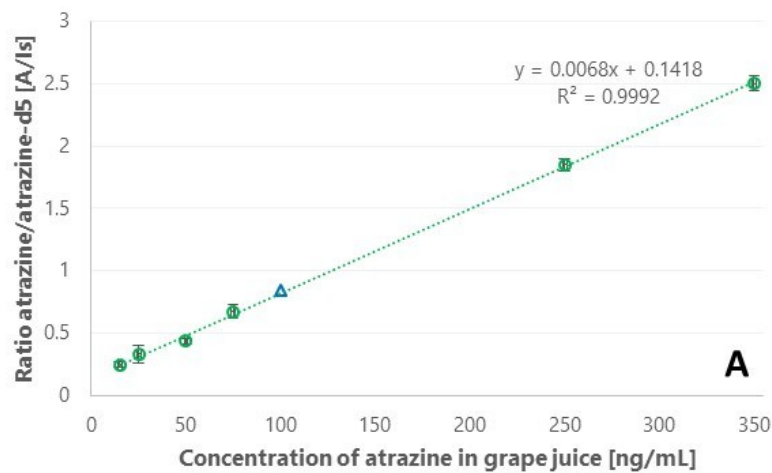[±] Equal contribution of authors

Figure S1 Semi-Quantitative analysis of Concord grape juice spiked with the following pesticides: (**A**) atrazine (15 ng ml^{-1} to 350 ng mL^{-1}); (**B**) pyraclostrobin (25 ng ml^{-1} to 500 ng mL^{-1}); and (**C**) azoxystrobin (25 ng ml^{-1} to 500 ng mL^{-1}). Atrazine-d^5 was used as the internal standard, and it was spiked at a fixed concentration in all samples (100 ng mL^{-1}).
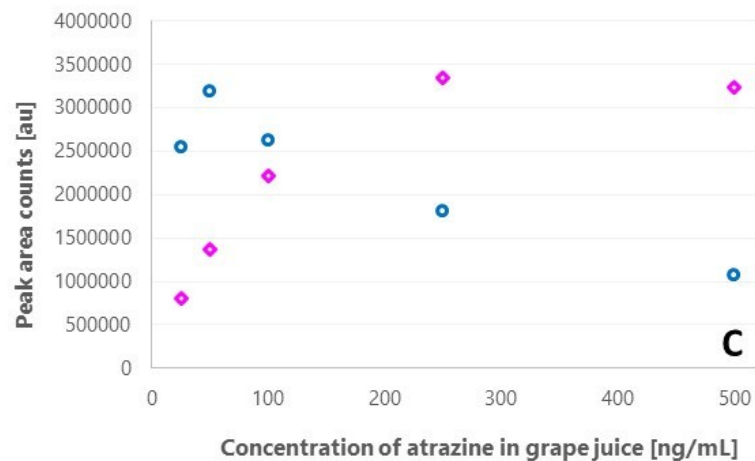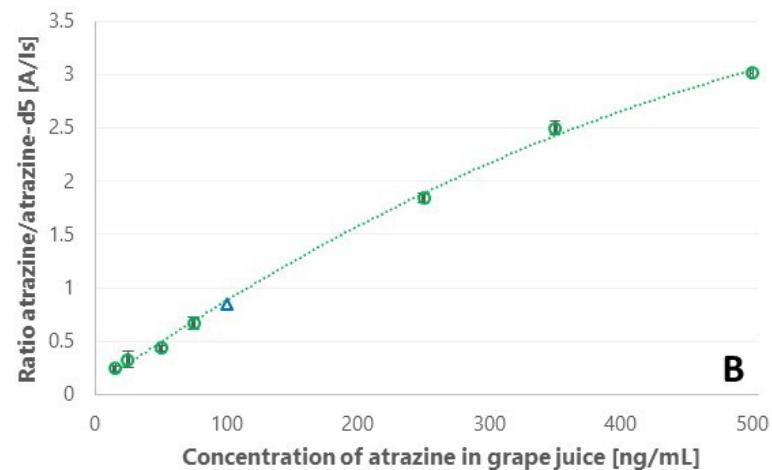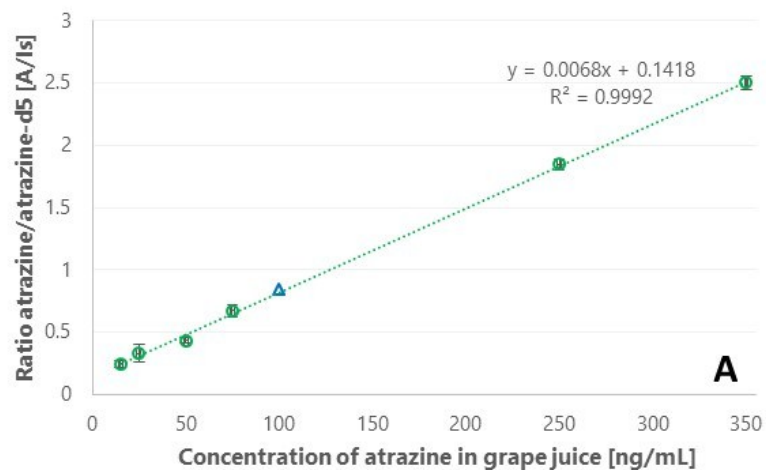
Figure S2 Semi-quantitative analysis of Concord grape juice spiked with atrazine: (**A**) atrazine (15 ng ml^{-1} to 350 ng mL^{-1}); (**B**) atrazine (15 ng ml^{-1} to 500 ng mL^{-1}); and (**C**) raw data of atrazine (pink diamonds) and atrazine-d^5 (blue circles). Atrazine-d^5 was used as the internal standard, and it was spiked at a fixed concentration in all samples (100 ng mL^{-1}).
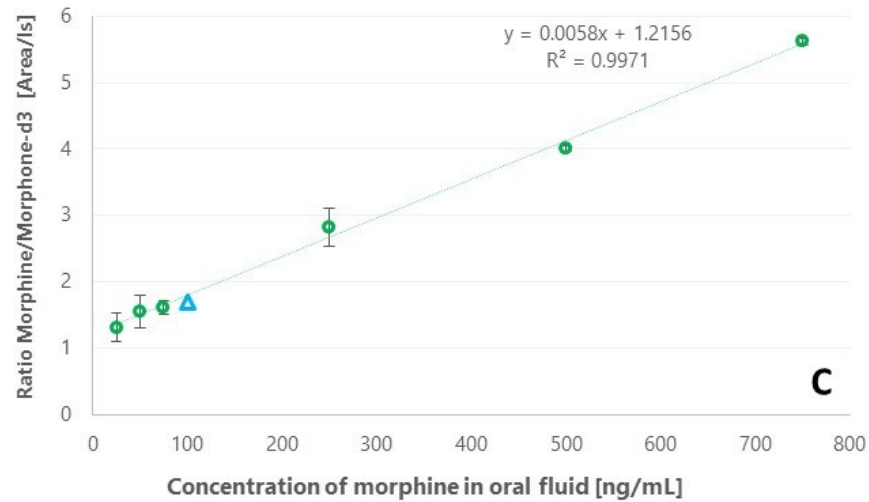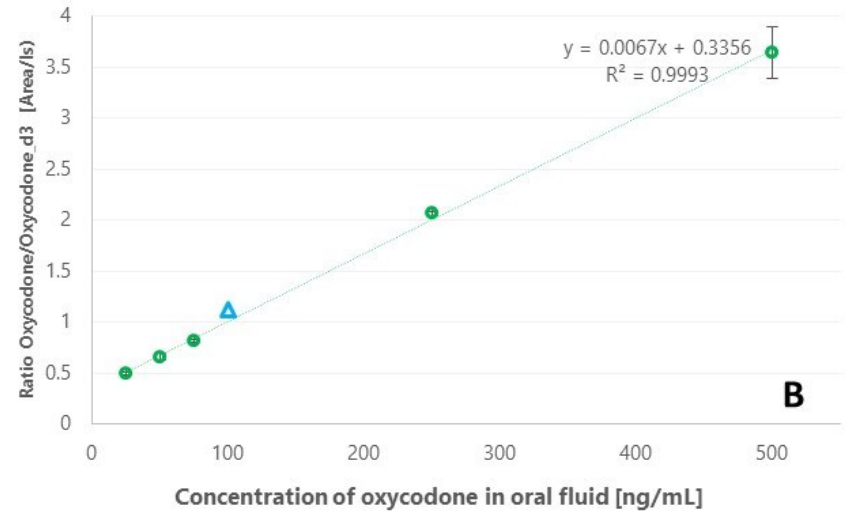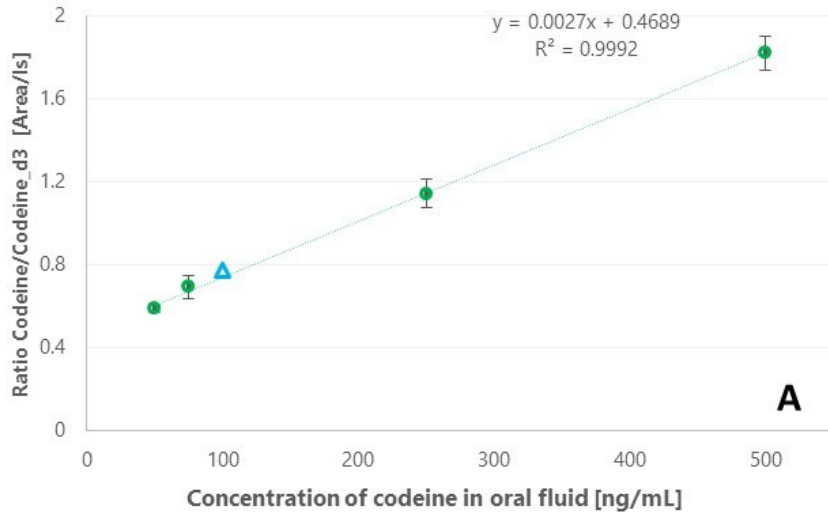
Figure S3 Semi-quantitative analysis of oral fluid spiked with the following drugs of abuse: (**A**) codeine (50 ng ml^{-1} to 500 ng mL^{-1}); (**B**) oxycodone (25 ng ml^{-1} to 500 ng mL^{-1}); and (**C**) morphine (25 ng ml^{-1} to 750 ng mL^{-1}). Deuterated analogues of each analyte were used as internal standards and were spiked at a fixed concentration in all samples (100 ng mL^{-1}).
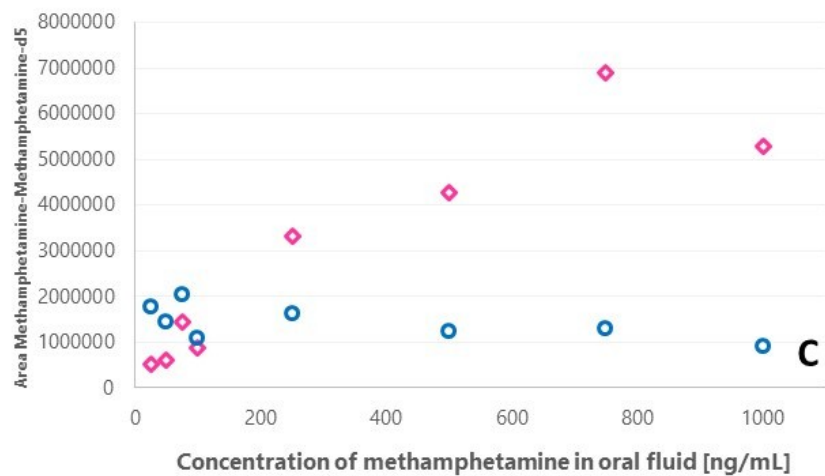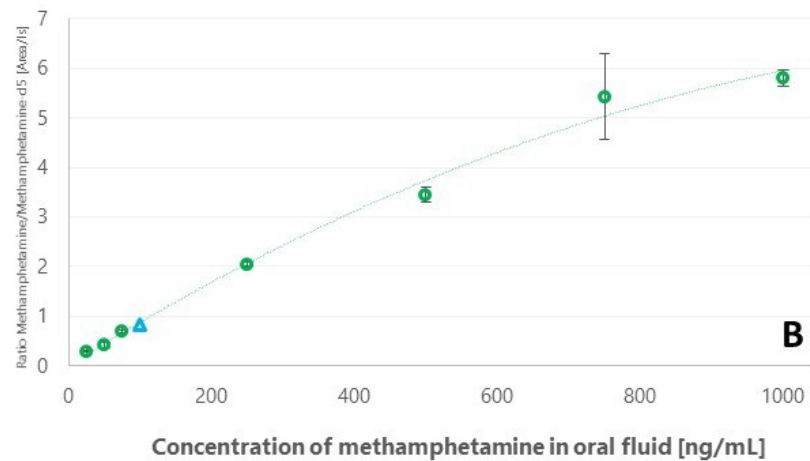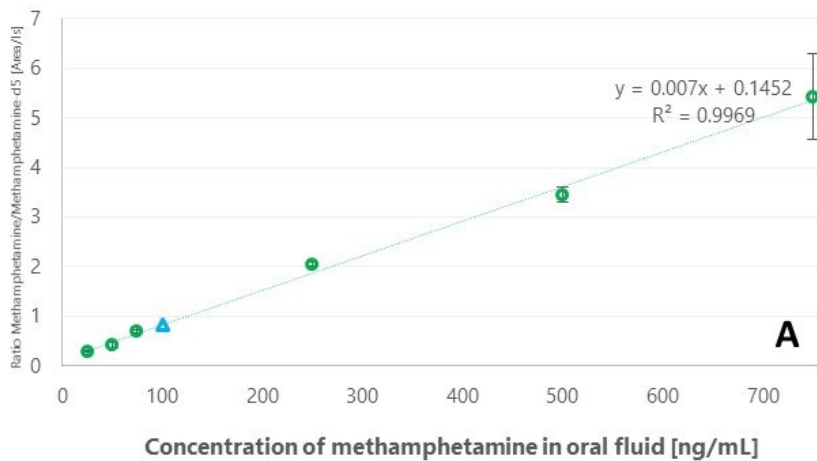
Figure S4 Semi-quantitative analysis of oral fluid spiked with methamphetamine: (**A**) methamphetamine (25 ng ml^{-1} to 750 ng mL^{-1}); (**B**) methamphetamine (25 ng ml^{-1} to 1000 ng mL^{-1}); and (**C**) raw data of methamphetamine (pink diamonds) and methamphetamine-d^5 (blue circles). Methamphetamine-d^5 was used as the internal standard, and it was spiked at a fixed concentration in all samples (100 ng mL^{-1}).
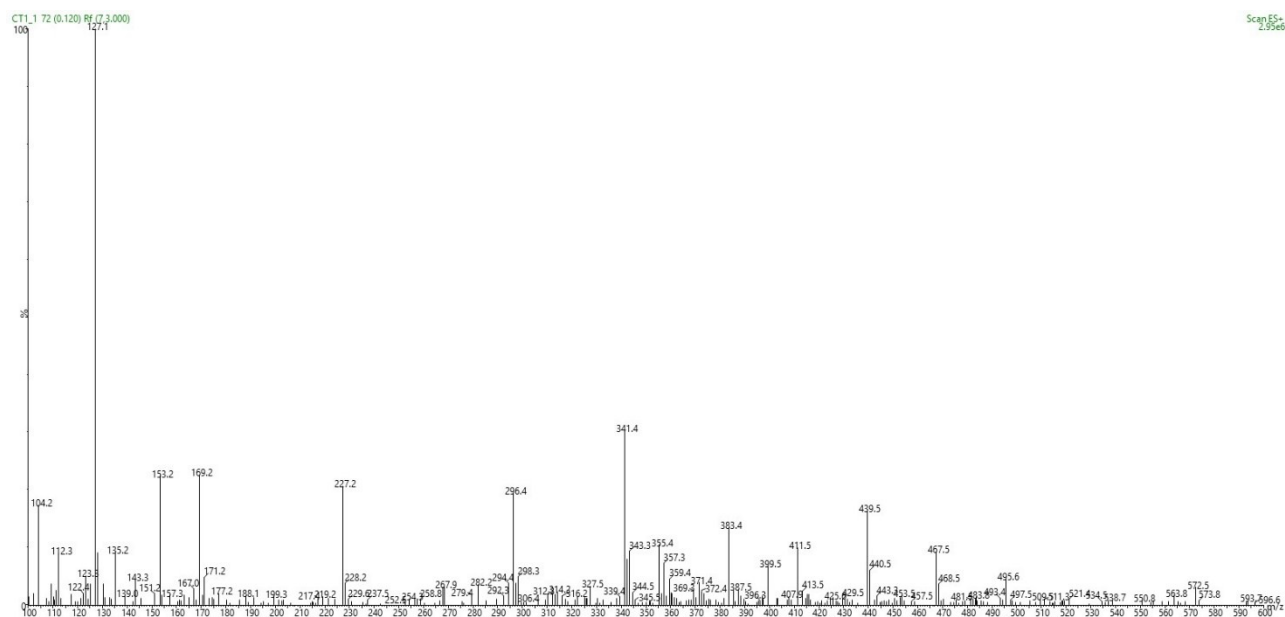
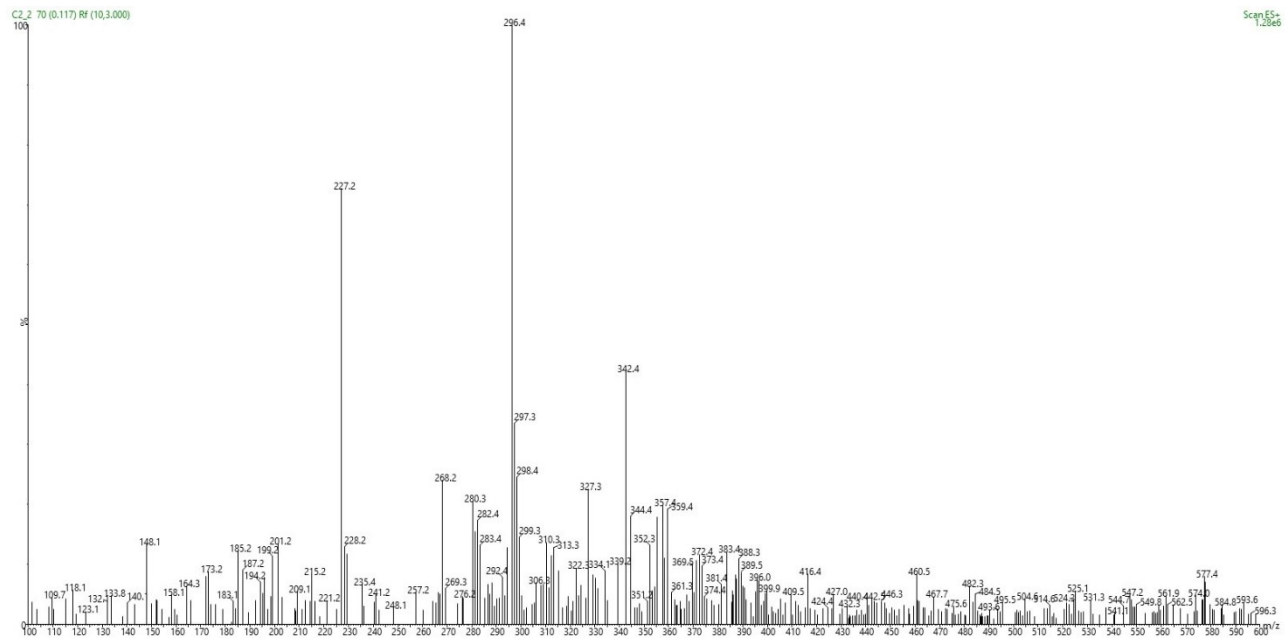**Figure S5** Mass spectra profile obtained after 1 min extraction from 1.5mL of coconut milk

Figure S6 Mass spectra profile obtained after 1 min extraction from 1.5mL of cow milk (2%, M.F.)
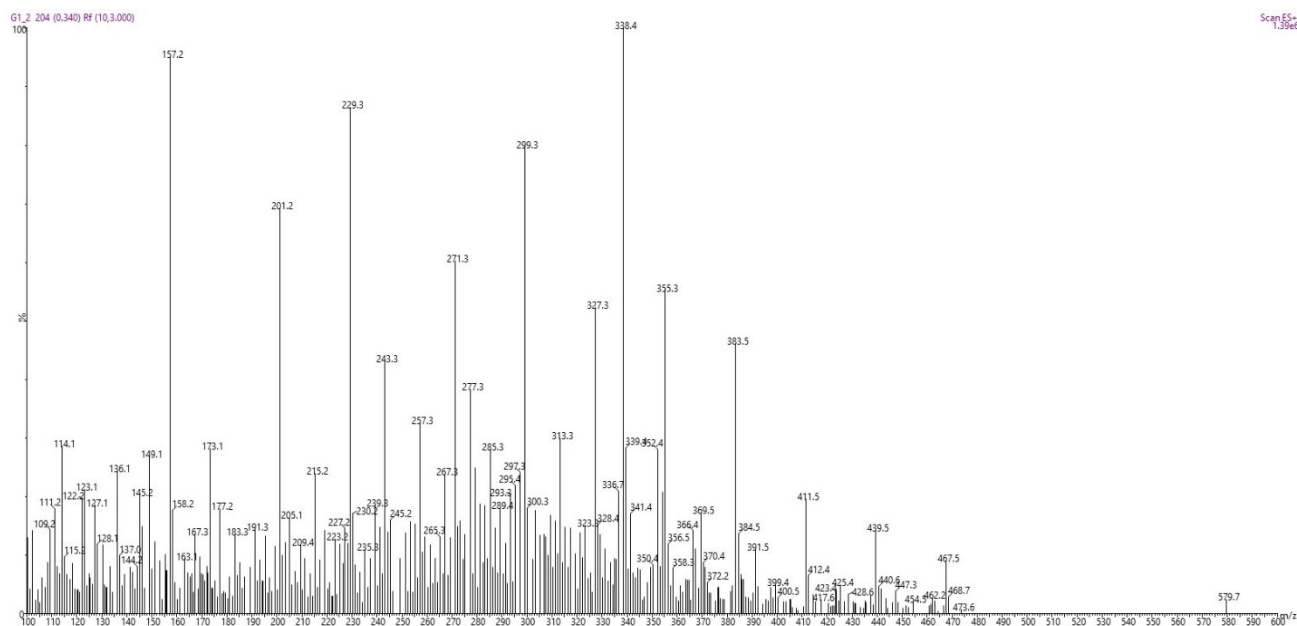
Figure S7 Mass spectra profile obtained after 1 min extraction from 1.5mL of goat milk
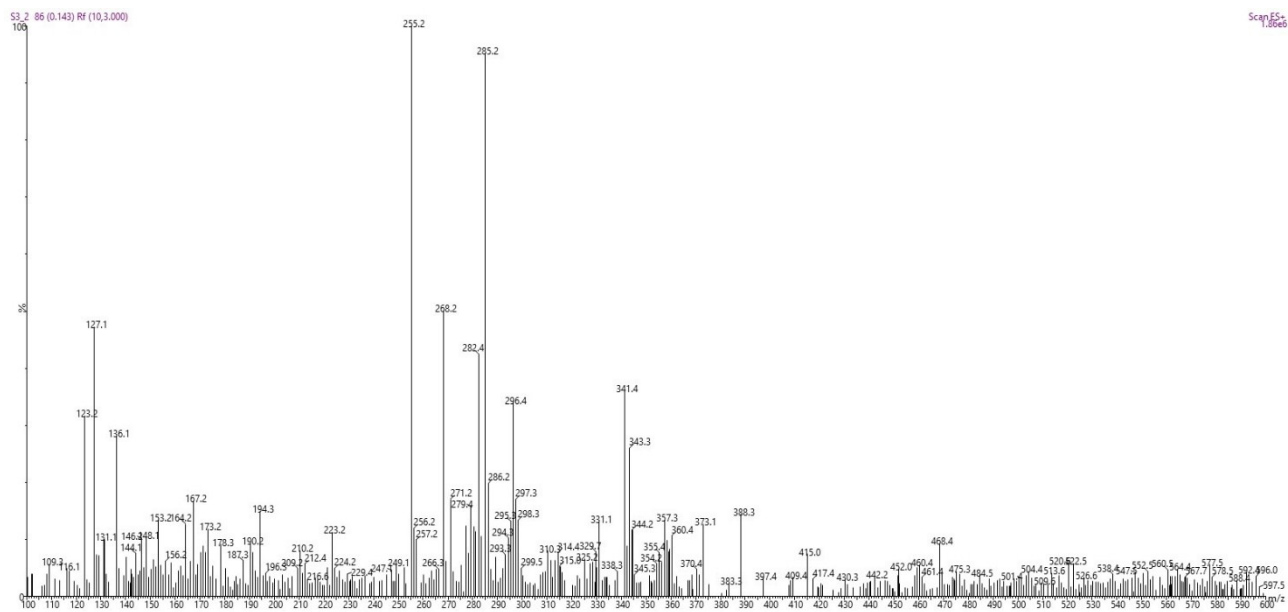

Figure S8 Mass spectra profile obtained after 1 min extraction from 1.5mL of soy milk
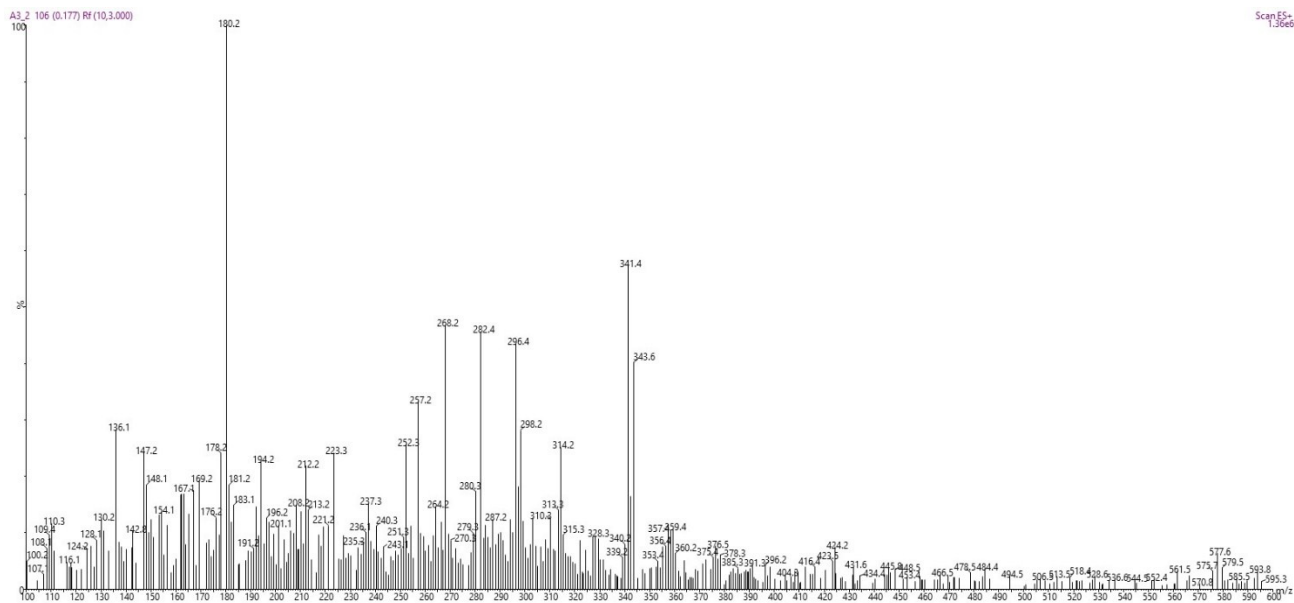
Figure S9 Mass spectra profile obtained after 1 min extraction from 1.5mL of almond milk
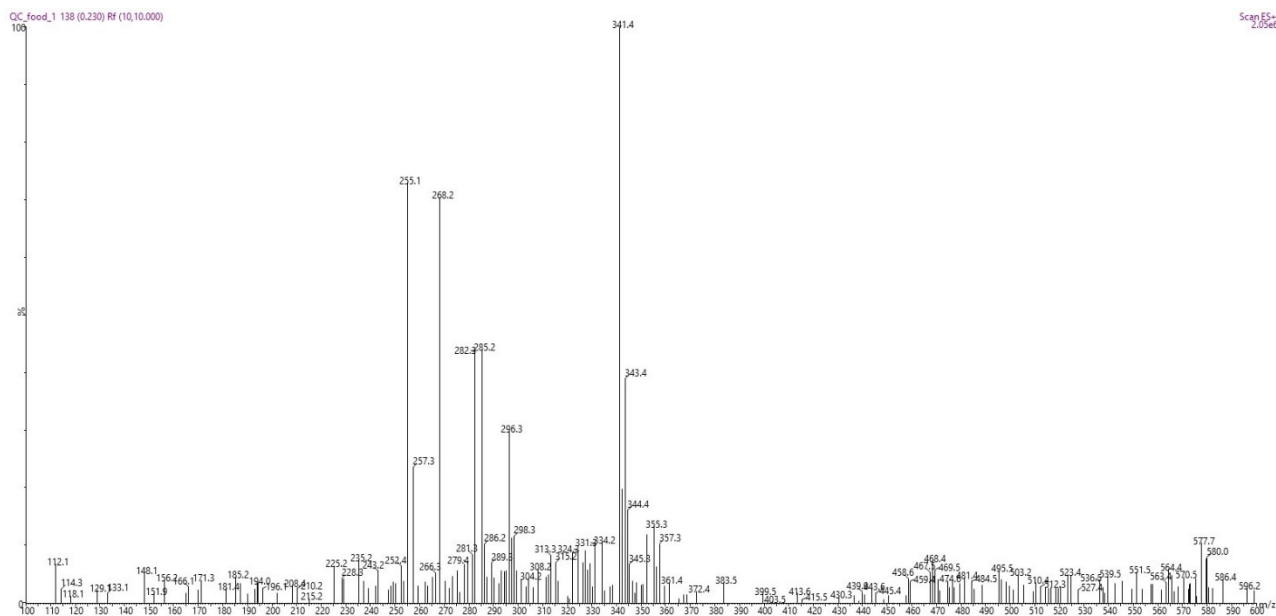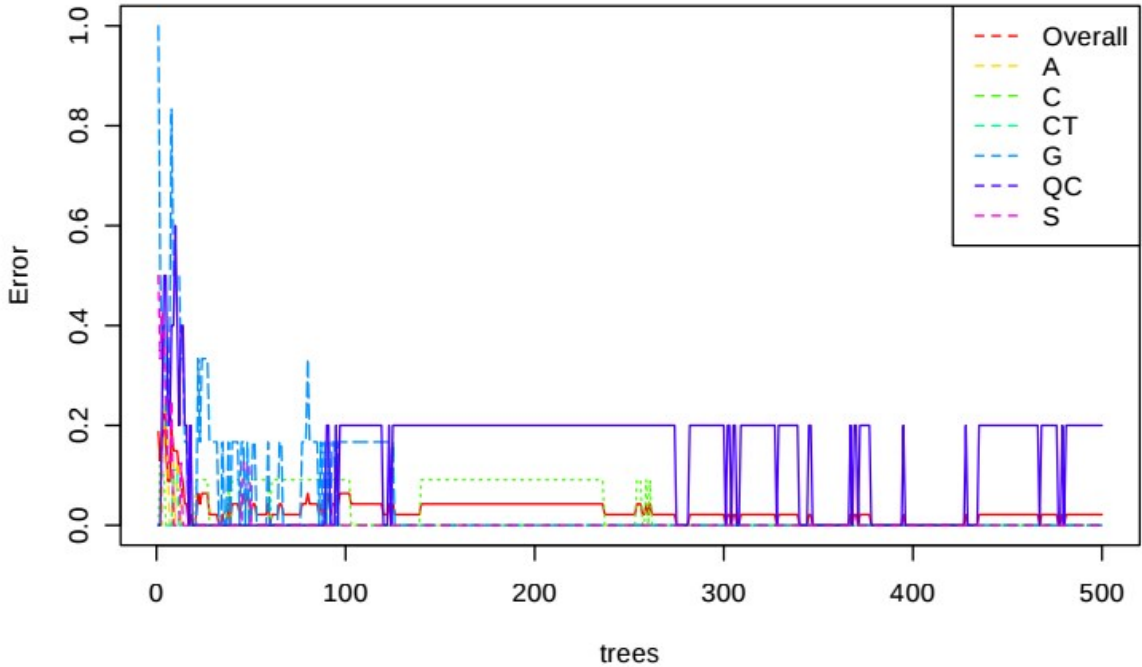

Figure S10 Mass spectra profile obtained after 1 min extraction from 1.5mL of QC-milk (mixture of all samples)

Random Forest classification

Class	A	C	CT	G	QC	S	Class Error
A	8	0	0	0	0	0	0
C	0	11	0	0	0	0	0
CT	0	0	9	0	0	0	0
G	0	0	0	6	0	0	0
QC	0	0	0	0	4	1	0.2
S	0	0	0	0	0	8	0

Figure S11 Cumulative error rates by Random Forest classification. The overall error rate is shown as the black line; the red and green lines represent the error rates for each class. Table on figure presents the confusion matrix of random forest. The out-of-bag (OOB) error is 0.0213. Figures and tables were generated using MetaboAnalyst 3.0.

Table S1 Nutritional facts of tested milks for untargeted molecular profiling

Samples	Fat* (g)	Carbohydrate* (g)	Sodium* (mg)	Protein (g)
Coconut milk #1	4.5	1	35	0
Coconut milk #2	4.7	1	26	0
Coconut milk #3	5.2	1	156	0
Cow milk #1	5	13	110	8
Cow milk #2	5	12	100	5
Cow milk #3	5	12	100	9
Cow milk #4	5	12	110	9
Goat milk #1	5	11	100	7
Almond milk #1	2.5	<1	160	1
Almond milk #2	2.5	13	180	1
Almond milk #3	3	1	110	1
Soy milk #1	4	8	90	6
Soy milk #2	4	4	75	7
Soy milk #3	4	8	115	1

*Content for 250 ml of beverage