

SUPPLEMENTARY CONTENT

Direct Analysis in Real Time - High resolution mass spectrometry as a valuable tool for polyphenols profiling in olive oil

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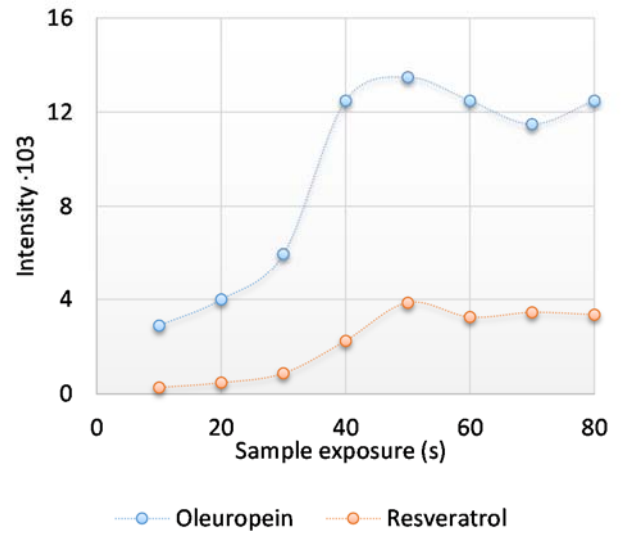
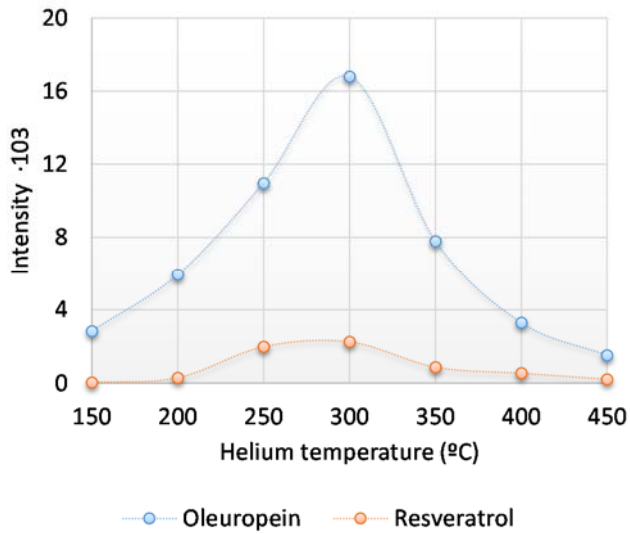
Table S1 Characteristics of the oil samples analyzed in the present study

Number	Type	Quality ¹	Origin	Variety	Data of consumption
1	Olive	EVOO	Spain	Not specified	August, 2015
2	Olive	EVOO	Cacerés, Extremadura (Spain)	Cacereña	March, 2015
3	Olive	EVOO	Andalusia (Spain)	Picual	August, 2015
4	Olive	EVOO	Andalusia (Spain)	Hojiblanca	September, 2015
5	Olive	VOO	Spain	Not specified	June, 2015
6	Sunflower	-----	-----	-----	-----
7	Sunflower	---	-----	-----	-----
8	Olive	EVOO	Spain	Not specified	July, 2015
9	Olive	OO	Spain	Not specified	Not specified
10	Maize	---	-----	-----	-----
11	Olive	OO	Spain	Arbequina	Not specified
12	Olive	EVOO	Lleida, Catalonia (Spain)	Arbequina, Verdells, Grossals	October, 2015
13	Olive	EVOO	Granada, Andalusia (Spain)	Not specified	March, 2015
14	Olive	EVOO	Emporda, Catalonia (Spain)	Agudell	June, 2015
15	Olive	EVOO	Andalusia (Spain)	Picual	July, 2015
16	Olive	EVOO	Lleida, Catalonia (Spain)	Arbequina, Picual	June, 2016
17	Olive	EVOO	Catalonia (Spain)	Arbequina, Picual	April, 2016
18	Olive	EVOO	Catalonia (Spain)	Arbequine, Argudell	November, 2014
19	Olive	EVOO	Alt Emporda, Catalonia (Spain)	Argudell	November, 2015
20	Olive	EVOO	Andalusia (Spain)	Picual	November, 2015
21	Olive	EVOO	Spain	Arbequine	July, 2015
22	Olive	EVOO	Catalonia (Spain)	Arbequine	Not specified
23	Olive	EVOO	Spain	Hojiblanca	January, 2016
24	Olive	EVOO	Andalusia (Spain)	Picual	July, 2016
25	Olive	EVOO	Andalusia (Spain)	Picual	July, 2015
26	Olive	EVOO	Andalusia (Spain)	Picual	July, 2015
27	Olive	EVOO	Spain	Picual	July, 2015
28	Olive	EVOO	Spain	Picual	November, 2015
29	Olive	EVOO	Spain	Not specified	December, 2015
30	Olive	EVOO	Segria, Catalonia (Spain)	Arbequine	Not defined
31	Olive	EVOO	Greece	Kalamata	Not defined
32	Olive	EVOO	Greece	Not specified	Not defined

¹ EVOO: extra virgin olive oil; VOO: virgin olive oil; OO: olive oil

Fig. S1 Deprotonated molecule $[M-H]^-$ intensity and its RSD against different DART conditions

A) Transmission-DART module



B) 12-Dip it

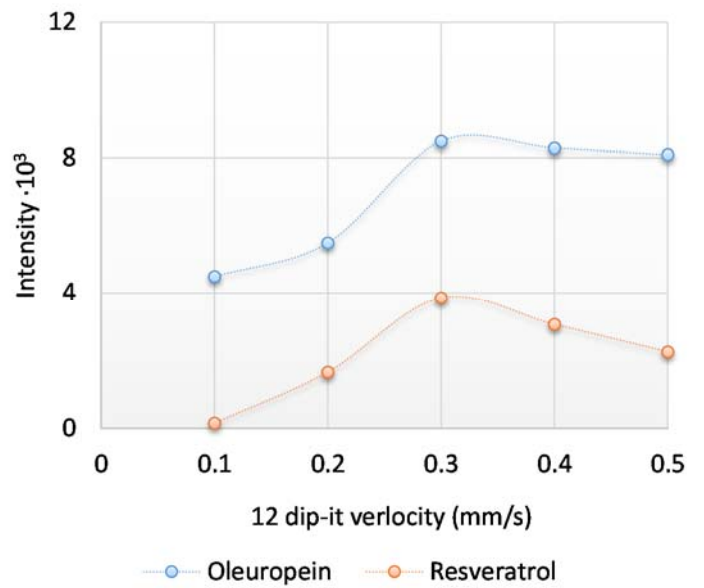
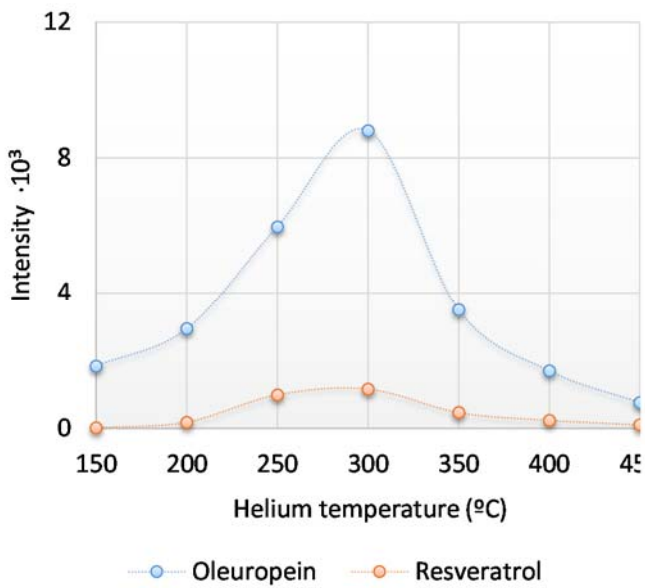


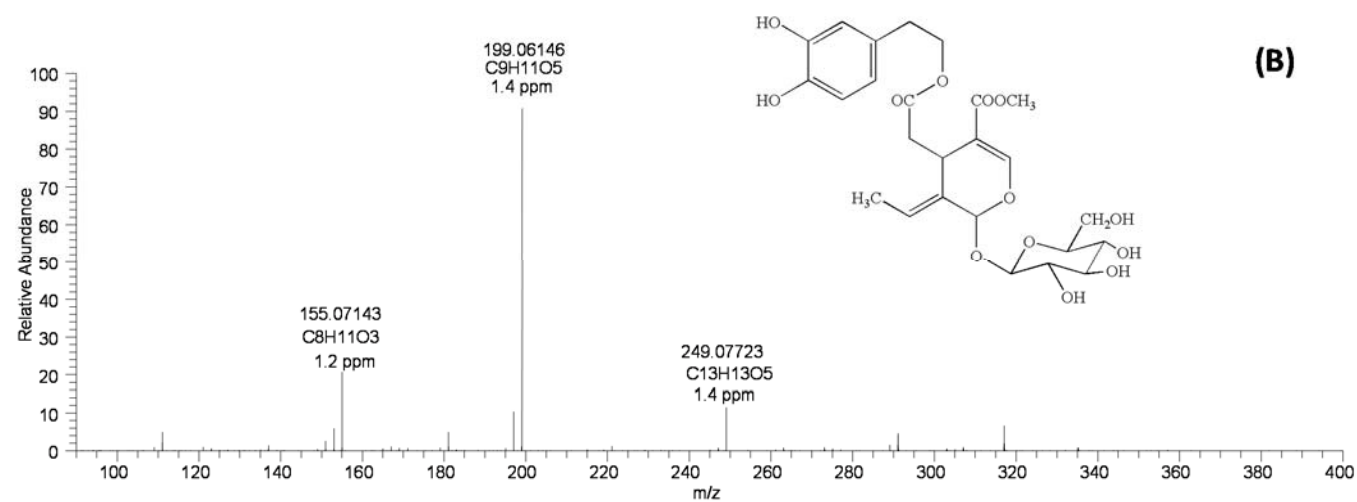
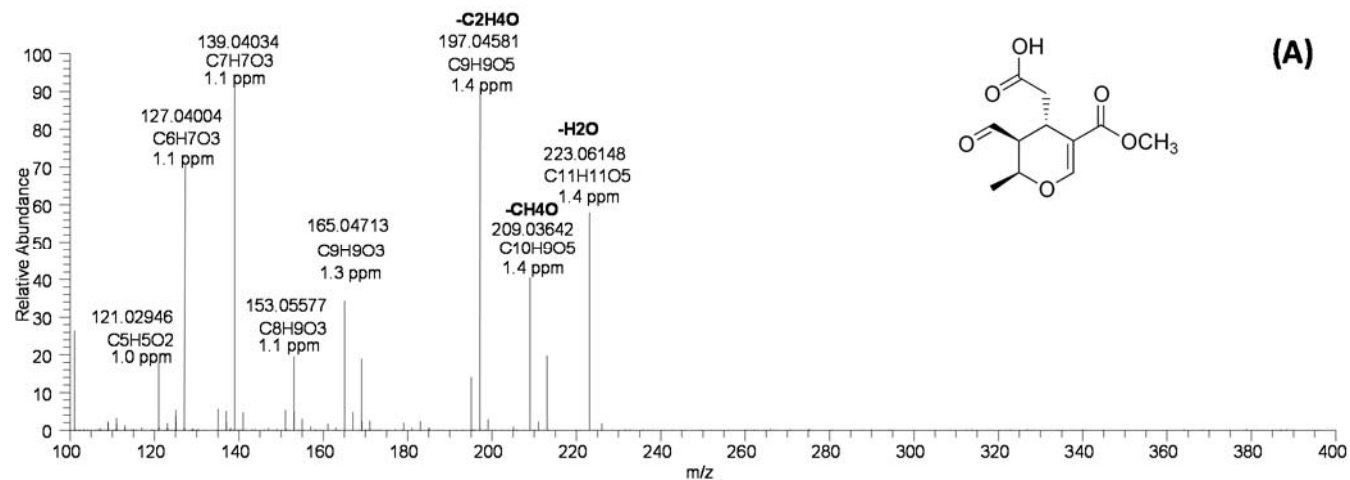
Table S2. Comparison of peak intensity and its RSDs ($n=10$) for 12-Dip it and transmission modules using the optimized conditions

Polyphenol	12-Dip it module		Transmission module	
	Peak area	RSDs	Peak area	RSDs
Resveratrol	1028572	15	1456298	8
Hydroxybenzoic acid	1529872	20	2272510	11
Vainillin	1402958	25	2587836	15
Hydroxytyrosol	2019485	22	2726530	10
Hydroxydecarboxymethyl elenolic acid	3420558	20	6638832	9
Elenolic acid	10485772	18	20841020	8
Oleuropein aglycone	12038528	15	26650368	7
Hydroxyelenolic acid	2598672	12	5368191	8
Ligstroside aglycone	2462985	15	4910304	7

Table S3. Resveratrol recoveries using different conditions to extract the compounds from an EVOO spiked at mg g⁻¹.

	Values of the conditions/recovery obtained				
Amount of sample (g)	0.5	1	1.5	2	
Recovery (%)	98	97	82	60	
Volume of hexane (mL)	0.5	1	1.5		
Recovery (%)	97	96	92		
Extractant	MeOH	AcN	H ₂ O	MeOH-H ₂ O (50:50 v/v)	AcN-H ₂ O (50:50 v/v)
Recovery (%)	85	75	80	97	87
% of MeOH-H ₂ O mixture	(25: 75)	(50:50)	(75:25)	(90:10)	
Recovery (%)	86	90	96	89	
Agitation time (min)	0.5	1	2	3	5
Recovery (%)	83	86	93	98	98
Centrifugation time (min)	2	3	4	5	
Recovery (%)	96	97	97	97	

Fig. S2 DART-Orbitrap-MS/MS identification of (A) Elenolic acid, (B) Hydroxydecarboxymethyl oleuropein aglycone and (C) Hydroxy oleuropein aglycone



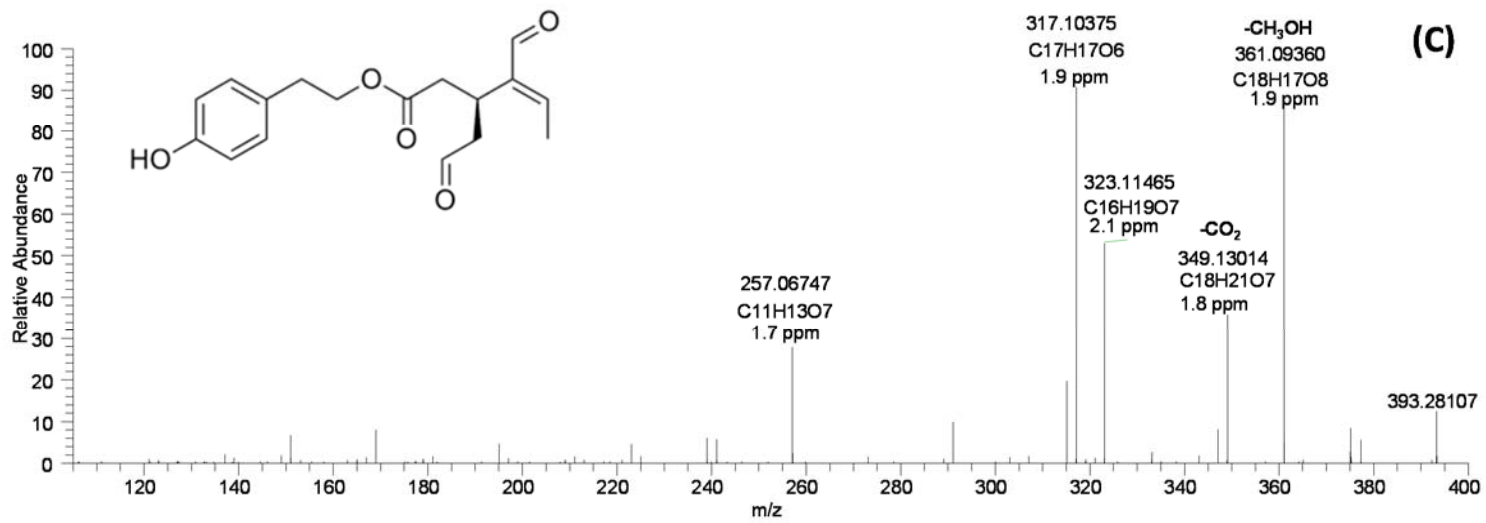


Fig. S3. DART-MS of EVOO 9

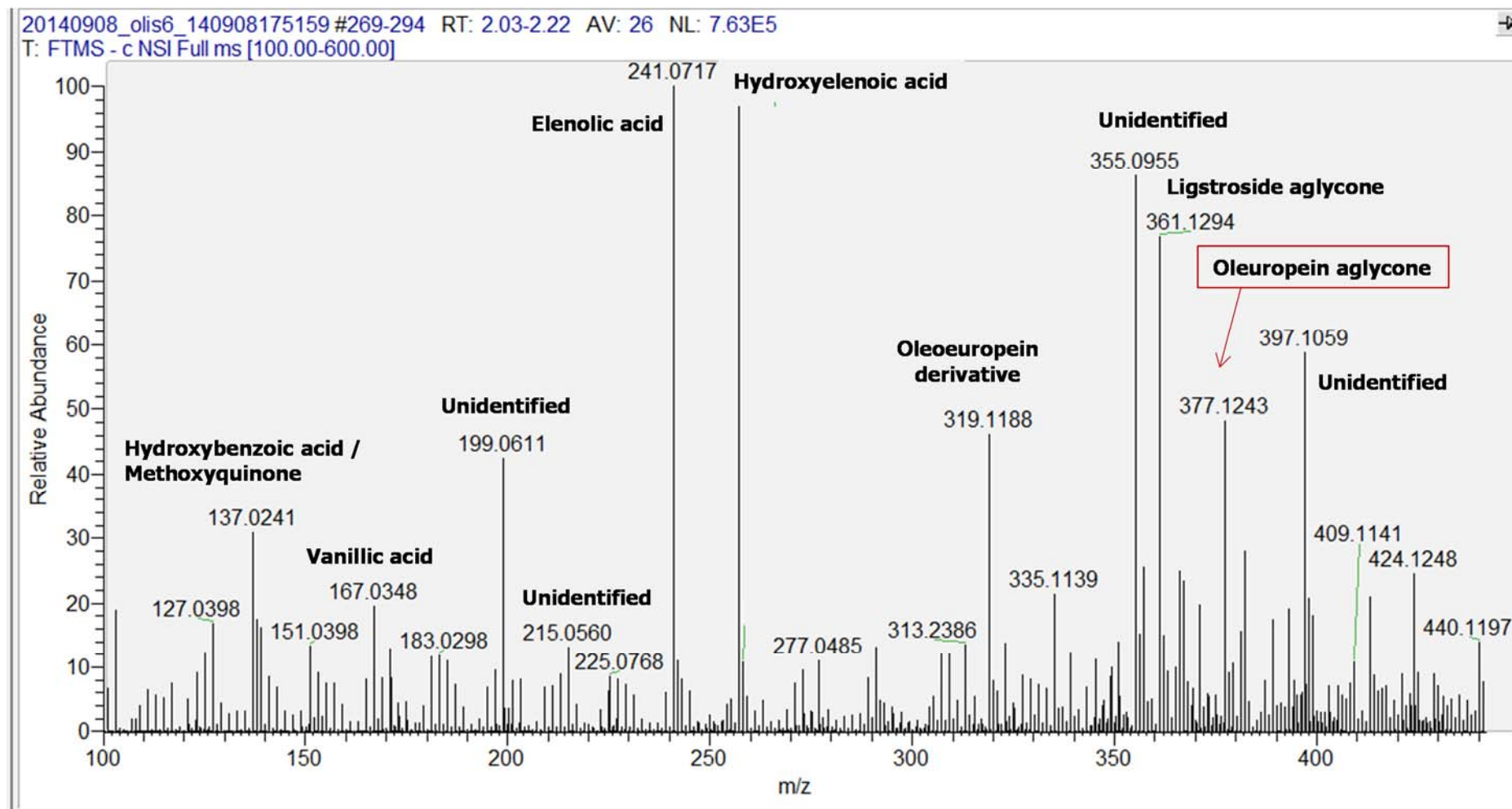


Fig S4 Detailed results of the method validation for resveratrol

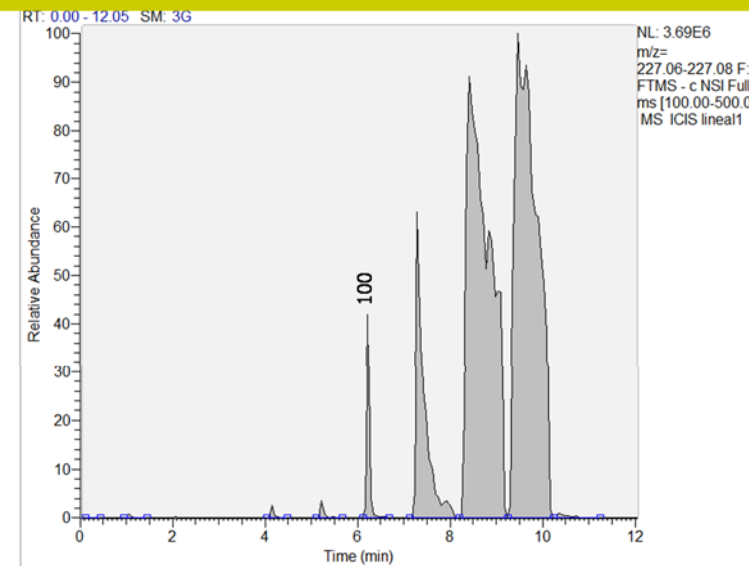
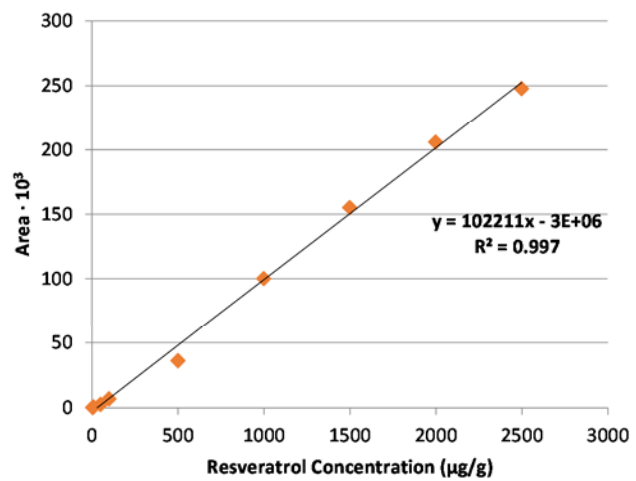
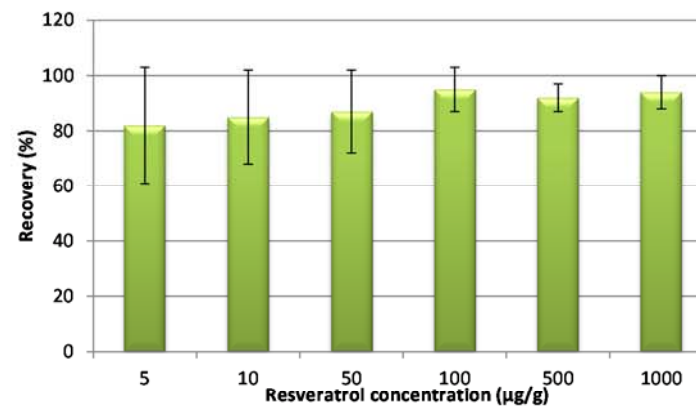
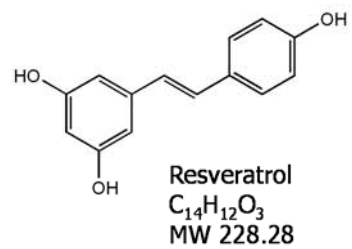
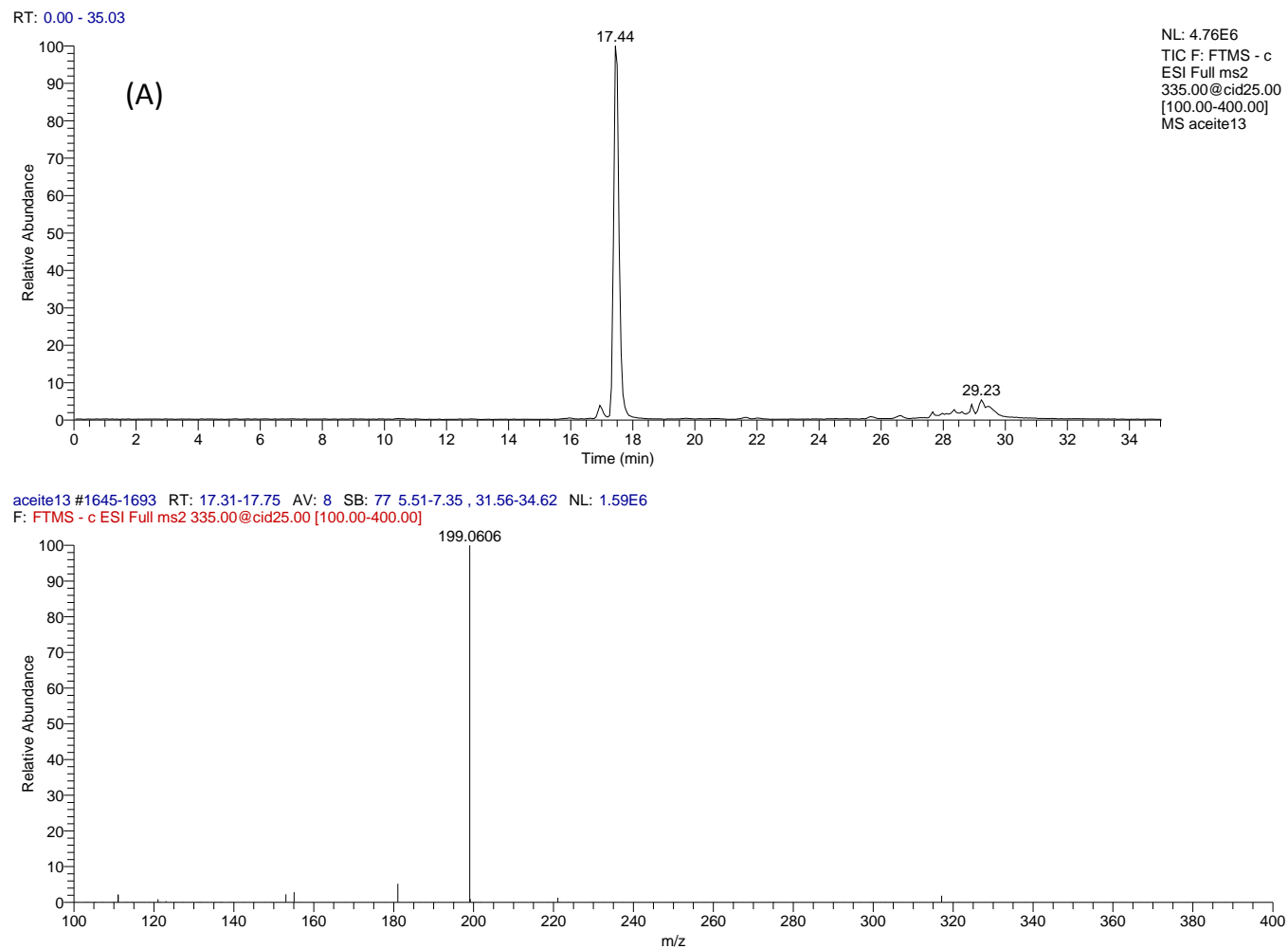


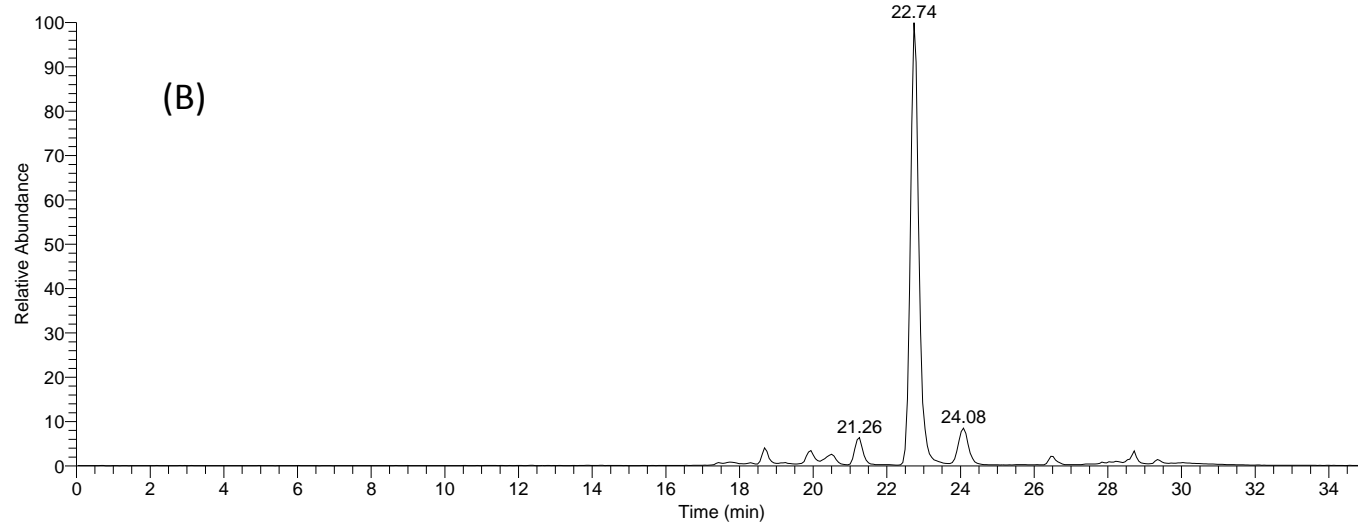
Table S4. Precision of the different main polyphenols ions intensity and masses (average values \pm RSDs) Various strategies have been adopted to remove arsenic from water sources, including oxidation/precipitation, coagulation, ion exchange, and membrane-based separation.

Intra-day precision ($n=10$)				Inter-day precision ($n=10$)			
Average (m/z)	RSD (%)	Ion Intensity	RSDs (%)	Average (m/z)	RSD (%)	Ion Intensity	RSDs (%)
137.03153	0.0010	573858	17	137.0315	0.0011	95692	23
139.02752	0.0009	565699	14	139.0274	0.0011	94332	21
151.03659	0.0006	447688	15	151.0368	0.0008	74667	19
153.03927	0.0017	525391	10	153.0383	0.0018	87618	13
165.03882	0.0024	529055	10	165.0395	0.0016	88232	14
167.03586	0.0015	457421	11	167.0371	0.0013	76294	14
169.04088	0.0040	367492	10	169.0402	0.0051	61307	14
181.03710	0.0015	446551	15	181.0358	0.0004	74488	18
183.05495	0.0018	563907	17	183.0543	0.0020	94048	24
185.05490	0.0073	372536	18	185.0485	0.0065	62154	22
187.06264	0.0007	299660	16	187.0631	0.0007	50008	22
195.05833	0.0017	397268	9	195.0571	0.0017	66278	12
199.06449	0.0014	641590	14	199.0639	0.0014	107000	22
241.07341	0.0003	2130069	11	241.0733	0.0004	355094	13
319.11496	0.0007	387097	15	319.1139	0.0005	64625	18
377.12428	0.0002	697108	17	377.1244	0.0002	116313	22

Fig S5 LC-Orbitrap MS/MS of (A) Hydroxydecarboxymethyl oleuropein aglycone and (B) Hydroxy oleuropein aglycone

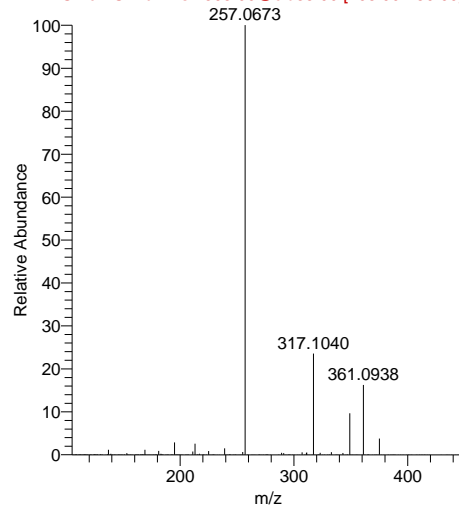


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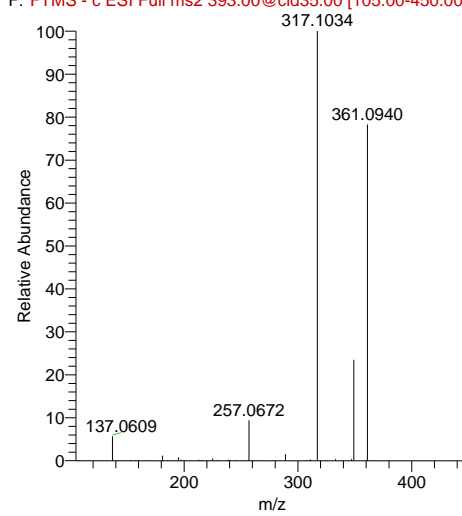


NL: 1.49E7
TIC F: FTMS - c
ESI Full ms2
393.00@cid35.00
[105.00-450.00]
MS aceite13

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F: FTMS - c ESI Full ms2 393.00@cid35.00 [105.00-450.00]



aceite13 #2009-2032 RT: 21.13-21.32 AV: 4 SB: 30
F: FTMS - c ESI Full ms2 393.00@cid35.00 [105.00-450.00]



aceite13 #2009-2032 RT: 21.13-21.32 AV: 4 SB: 30
F: FTMS - c ESI Full ms2 393.00@cid35.00 [105.00-450.00]

