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Supplementary Material

Gas and Liquid Chromatography Mass Spectrometry as a Tool for Elucidating Volatile Organic Compounds (VOCs) and Metabolites in Maternal Milk: A Perspective on Infants' Health Risk Assessment

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Table S1. Accuracy (mean recovery, n=5) and precision (n=5) at 3×LLOQ, 30×LLOQ and ULOQ.

Compound	LLOQ (ng mL^{-1})	Mean Recovery (3×LLOQ) ±RSD %	Precision (3×LLOQ) %CV	Mean Recovery (30×LLOQ) ±RSD %	Precision (30×LLOQ) %CV	Mean Recovery (ULOQ) ±RSD %	Precision (ULOQ) %CV
Isoprene	0.1	82±14	10	87±13	12	90±10	7
2-Methyl pentane	1	82±13	11	91±7	11	86±8	4
Methyl tert-butyl-ether	1	83±8	8	88±11	8	87±13	5
Hexane	0.5	91±15	7	86±8	11	82±14	12
Dichloromethane	0.2	92±10	9	90±14	10	88±7	15
Tetrahydrofuran	1	98±9	12	91±15	7	81±9	8
Benzene	0.2	81±11	15	85±11	7	90±12	9
Heptane	0.5	84±9	13	82±7	12	85±14	14
Octane	0.2	91±11	9	83±10	11	86±8	8
2,2,4-Trimethyl pentane	1	85±12	6	91±11	7	94±9	10
Toluene	0.2	91±14	12	94±10	12	92±13	10
1,3-Dichloropro-pene	1	85±11	12	79±11	16	88±8	15
1,1,2-Trichloro-ethane	1	90±13	10	81±12	9	84±10	14
Tetrachloroeth-ylene	0.5	82±13	8	93±9	7	93±9	4
Chlorobenzene	0.5	92±12	13	91±12	12	90±10	13
Ethyl benzene	0.5	85±9	15	88±12	13	87±5	11
p-Xylene	0.2	89±10	12	87±10	6	91±12	4
m-Xylene	0.2	89±11	11	81±12	5	80±5	7
o-Xylene	0.5	93±9	10	87±8	4	83±11	5
Styrene	0.2	84±9	5	89±10	11	82±5	6
1,2,4-Trimethyl benzene	0.5	92±10	6	92±11	10	94±7	12
1,2,3-Trimethyl benzene	0.5	87±11	6	91±13	8	90±8	10
p-Dichlorobenzene	0.2	87±15	9	88±9	14	80±12	15
1,2-Dichloroethene	1	77±10	10	83±11	12	88±9	15
1,2-Dichloroethane	1	86±8	13	88±9	8	91±6	5
Metabolite	**LLOQ (ng mL^{-1})**	**Mean Recovery (3×LLOQ) ±RSD %**		**Mean Recovery (30×LLOQ) ±RSD %**		**Mean Recovery (ULOQ) ±RSD %**	
DL-MA	0.5	90±12	12	87±11	12	89±13	9
R-MA	0.5	94±9	11	82±8	13	90±14	10
PGA	0.4	85±10	5	87±11	10	87±12	7
2-MHA	0.4	81±12	7	87±12	9	88±8	5
3-MHA	0.4	90±12	12	82±8	15	87±11	13
4-MHA	0.4	85±12	10	83±7	9	88±7	11
BMA	0.2	90±9	7	92±15	6	87±11	4
PMA	0.2	92±11	8	87±9	11	94±9	7
HA	0.4	106±14	8	101±10	16	98±14	12

Table S2. Accuracy (mean recovery, n=5) and precision (n=5) concerning the back-calculated concentrations of the calibration standards at LLOQ, 3×LLOQ, 30×LLOQ and ULOQ.

Compound	Mean Recovery (LLOQ) ±RSD %	Precision (LLOQ) %CV	Mean Recovery (3×LLOQ) ±RSD %	Precision (3×LLOQ) %CV	Mean Recovery (30×LLOQ) ±RSD %	Precision (30×LLOQ) %CV	Mean Recovery (ULOQ) ±RSD %	Precision (ULOQ) %CV
Isoprene	81±9	8	82±14	10	87±13	12	90±10	7
2-Methyl pentane	87±9	10	82±13	11	91±7	11	86±8	4
Methyl tert-butyl-ether	83±9	12	83±8	8	88±11	8	87±13	5
Hexane	92±13	18	91±15	7	86±8	11	82±14	12
Dichloro-methane	93±11	15	92±10	9	90±14	10	88±7	14
Tetrahy-drofuran	101±9	9	98±9	12	91±15	7	81±9	8
Benzene	80±9	7	81±11	15	85±11	7	92±12	9
Heptane	83±12	14	84±9	13	82±7	12	85±12	14
Octane	87±11	11	91±11	9	83±10	11	86±8	8
2,2,4-Tri-methyl pentane	92±8	14	83±12	6	91±11	7	94±9	10
Toluene	91±9	16	90±14	14	94±10	12	92±13	10
cis-1,3-Di-chloropro-pene	80±7	15	82±11	14	79±11	14	88±8	15
1,1,2-Tri-chloro-ethane	81±9	15	90±13	10	81±12	9	84±10	14
Tetrachlo-roethylene	85±6	18	82±13	8	93±9	7	93±9	4
Chloroben-zene	91±7	7	92±12	13	87±12	12	95±7	13
Ethyl ben-zene	89±10	12	85±9	14	88±12	13	87±5	11
p-Xylene	81±11	8	91±10	12	88±8	6	91±12	4
m-Xylene	89±14	6	87±8	11	81±12	9	80±8	7
o-Xylene	91±8	12	93±9	10	87±8	4	83±11	5
Styrene	84±8	15	84±9	5	89±10	11	82±5	6
1,2,4-Tri-methyl benzene	90±10	6	91±7	6	92±11	10	94±7	12
1,2,3-Tri-methyl benzene	89±14	7	87±11	6	91±13	8	90±8	10
p-Dichlo-robenzene	83±8	16	87±15	9	88±9	12	80±12	12

1,2-Dichloroethene	80±9	17	77±10	10	85±11	12	91±12	13
1,2-Dichloroethane	81±8	12	86±8	13	88±9	8	91±6	5
Metabolite	**Mean Recovery (LLOQ) ±RSD %**	**Precision (LLOQ) %CV**	**Mean Recovery (3×LLOQ) ±RSD %**	**Precision (3×LLOQ) %CV**	**Mean Recovery (30×LLOQ) ±RSD %**	**Precision (30×LLOQ) %CV**	**Mean Recovery (ULOQ) ±RSD %**	**Precision (ULOQ) %CV**
DL-MA	84±15	15	85±12	12	87±11	12	89±9	10
R-MA	87±14	14	91±10	10	82±8	13	90±14	10
PGA	91±10	7	83±14	9	87±11	10	87±12	7
2-MHA	80±11	9	86±12	9	87±12	9	88±8	5
3-MHA	85±8	10	90±12	12	87±13	13	87±11	14
4-MHA	91±11	8	85±12	10	83±6	9	93±7	11
BMA	86±12	6	90±9	7	92±15	6	87±8	4
PMA	82±5	11	92±11	8	87±9	11	94±9	7
HA	86±7	8	106±14	8	98±10	16	101±16	13

Table S3. Exemplary MS fragments, retention time (RT) and retention index (RI) for selected detected identified compounds.

Compound	MS Fragments	RT (min)	RI*
4-Mercaptophenol	126, 97, 53	17.78	1217
Citronellol	95, 69, 55, 41	18.59	1240(1232)
Diisobutyl phthalate	149, 121, 104, 76	30.85	1871(1869)
Phthalic acid, isobutyl neopentyl ester	223, 149, 167, 104	36.53	1968
4,4'-(1,3-Dimethylbutylidene)bisphenol	213, 165, 152, 119	40.31	2287
Bisphenol B, acetate	213, 165, 152, 119, 107	40.37	2294
Phthalic acid, decyl neopentyl ester	167, 149, 71	43.42	2639

* RI, retention index on Mega-5HT (30 m, 0.25 mm, 0.25 μm) column (relative to *n*-alkanes), identification based on mass spectra comparison with the reference databases and comparison (where applicable) with literature RIs (depicted in parentheses).

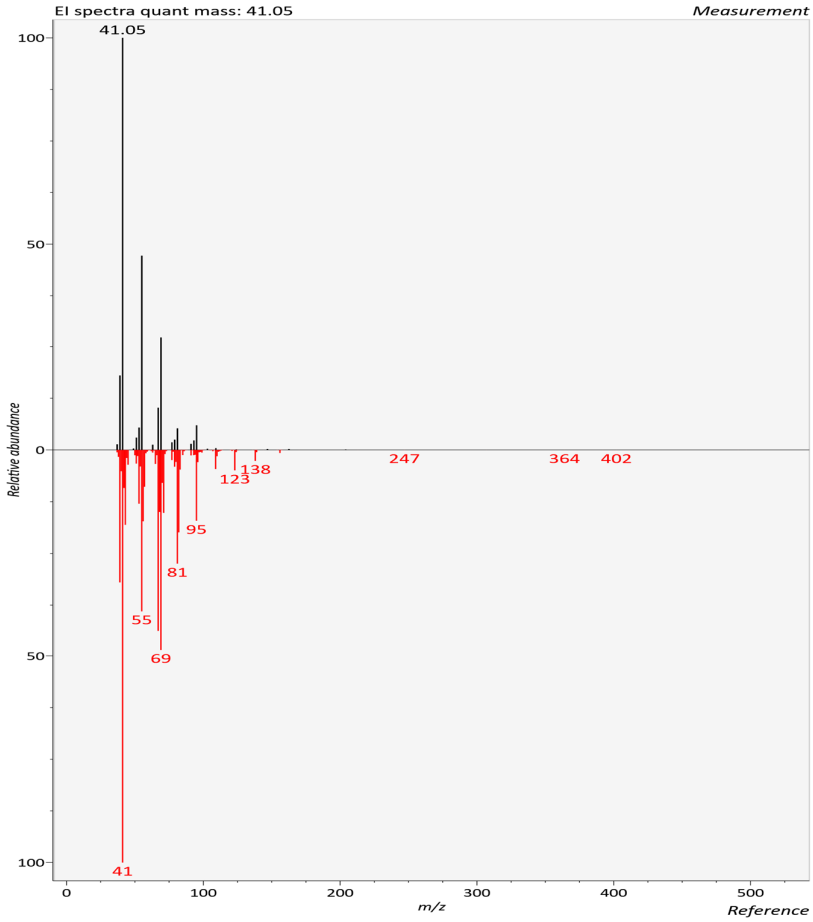

Figure S1. GC-MS full-scan spectra of citronellol in positive maternal milk sample (the top spectra corresponds to the one obtained in the maternal milk sample, while the spectra below corresponds to the respective of the NIST library).

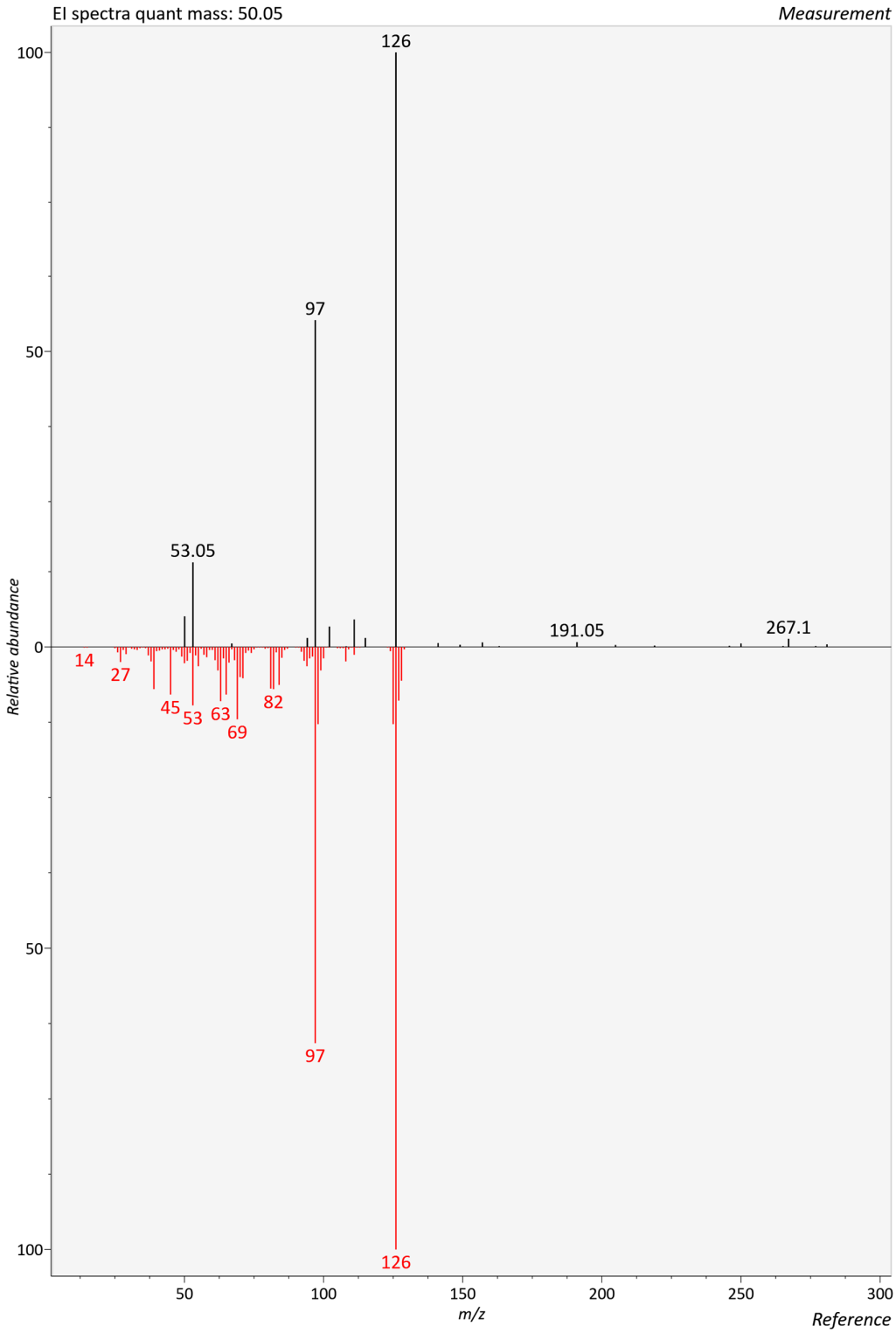

Figure S2. GC-MS full-scan spectra of 4-mercaptophenol in positive maternal milk sample (the top spectra corresponds to the one obtained in the maternal milk sample, while the spectra below corresponds to the respective of the NIST library).

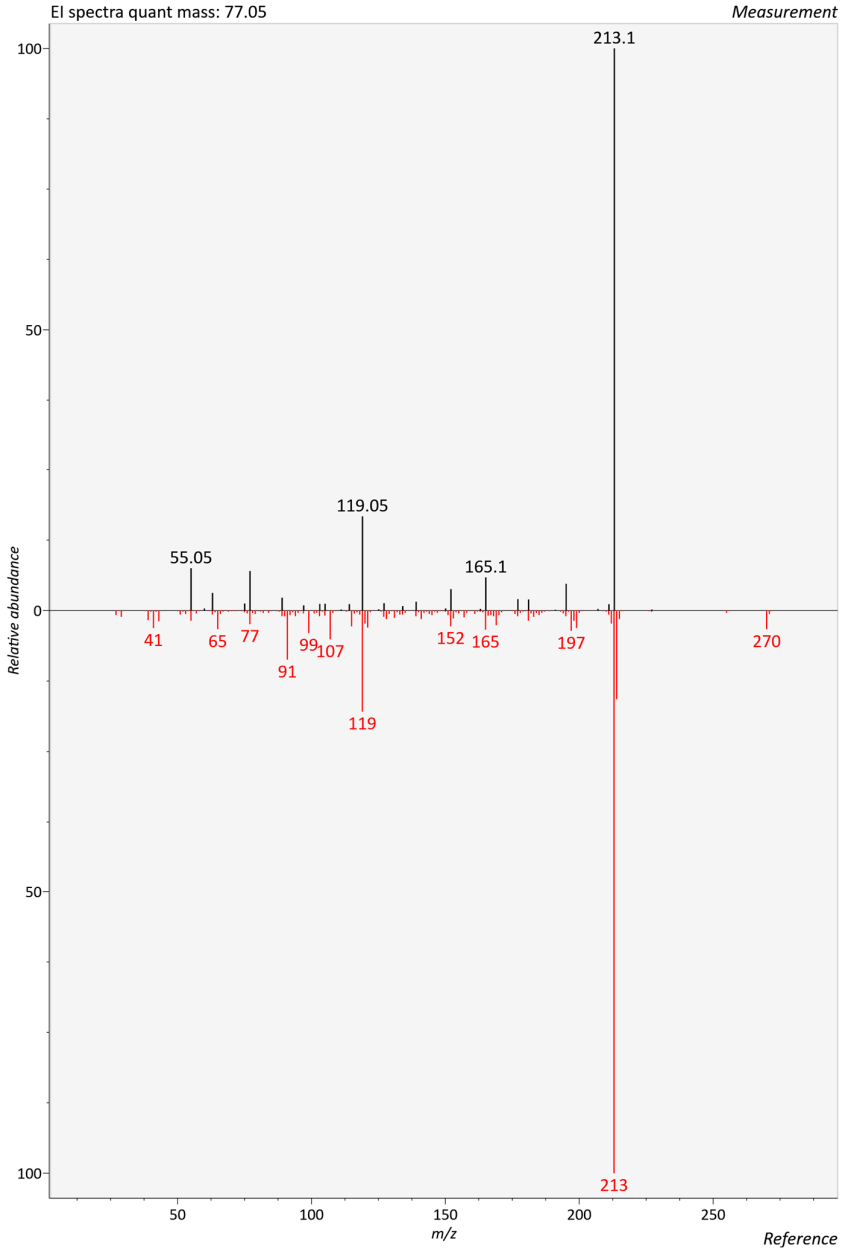

Figure S3. GC-MS full-scan spectra of 4,4'-(1,3-dimethylbutylidene)bisphenol in positive maternal milk sample (the top spectra corresponds to the one obtained in the maternal milk samples, while the spectra below corresponds to the respective of the NIST library).

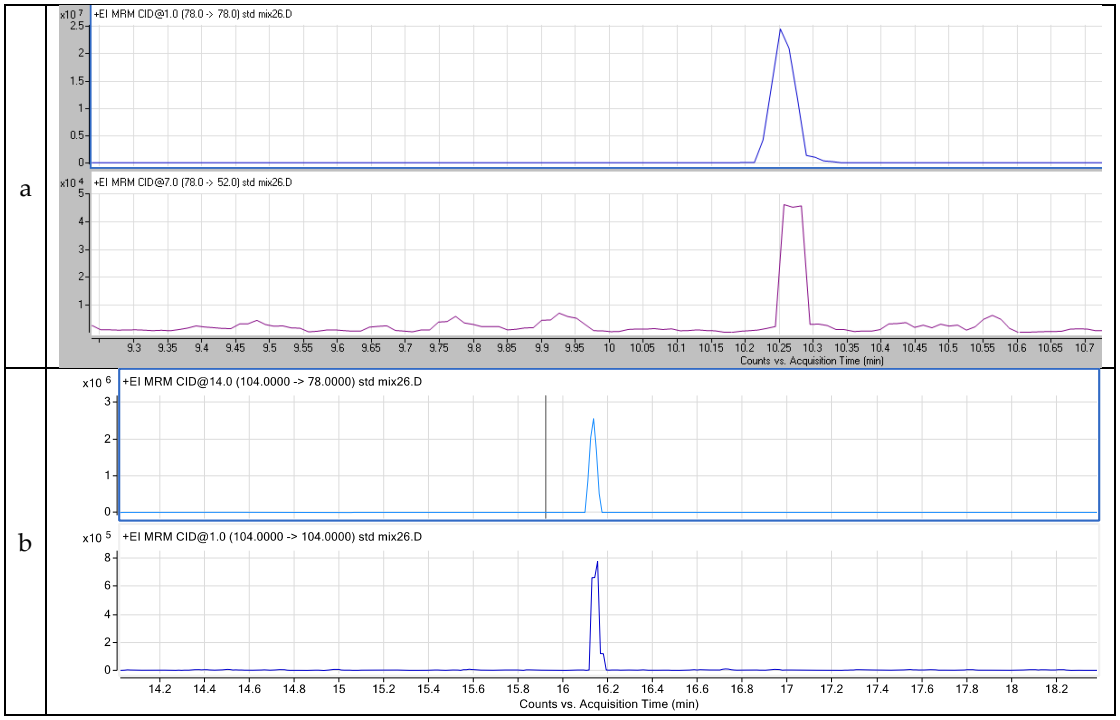

Figure S4. SRM transitions for benzene (a) and styrene (b) in standard mix in CS_2 at 10 ng mL^{-1}.