

# CONTROL OF MIGRANTS FROM PLASTIC PACKAGES TO HONEY SAMPLES USING TARGETED AND UNTARGETED ANALYSIS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY



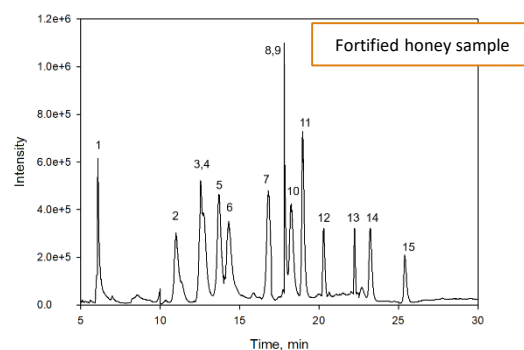
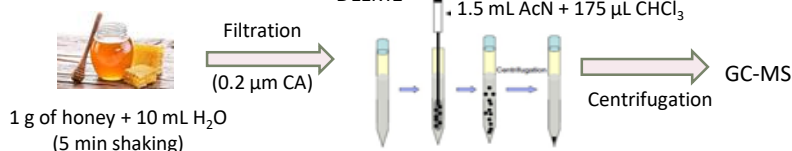
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**INTRODUCTION:** Honey is a natural high-quality product considered as a functional food due to its nutritional and medicinal properties. These recognized beneficial properties have led to its increasing consumption and make the quality control of honey of great importance. In this work, targeted and untargeted analysis by dispersive liquid-liquid microextraction (DLLME) followed by gas chromatography-mass spectrometry (GC-MS) is proposed to monitor potential migrants from polystyrene (PS) and polyethylene terephthalate (PET) honey plastic packaging.

## Sample treatment

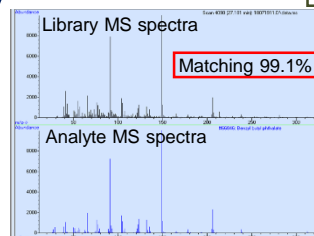


## TARGETED APPROACH

RETENTION TIME, TARGET AND QUALIFIER IONS FOR ALL THE ANALYTES

Compound	$t_r$ (min)	Target ( $m/z$ )	Q1 ( $m/z$ )	Q2 ( $m/z$ )
Styrene (1)	5.9	104	78	51
p-tert-butylphenol (2), p-TBP	10.6	135	150	136
Butyl hydroxyanisole (3), BHA	12.1	165	137	180
Pentylphenol (4), PP	12.4	107	108	164
2-tert-butyl-4-methylphenol (5), TBMP	12.7	205	57	220
Hexylphenol (6), HP	13.2	107	108	178
Diethyl phthalate (7), DEP	13.7	149	177	105
Tert-octylphenol (8), TOP	13.9	135	107	206
Octylphenol (9), OP	16.3	107	108	206
Nonylphenol (10), NP	17.7	107	108	220
Dibutyl phthalate (11), DBP	17.8	149	223	205
Oleamide (12)	20.5	55	69	282
Bisphenol A (13), BPA	21.3	213	228	270
Butyl benzyl phthalate (14), BBP	23.0	149	91	206
Diethylhexyl phthalate (15), DEHP	25.4	149	167	279

## UNTARGETED APPROACH



## Identified migrants in the samples

- Isobutyl phthalate
- Squalene
- Hexadecanoic acid
- Methyl palmitate
- Glycerol- $\beta$ -monostearate
- Hexadecanal
- Nonanoic acid
- Decanoic acid
- Stearic acid,
- Methyl stearate
- Phthalic anhydride
- 2,4-di-tert-butylphenol
- 9-di-tert-butyl-1-oxaspiro[4.5] deca-6,9-diene-2,8-dione

Home-made database (84 plastic related compounds)  $\rightarrow$  MS-Electron Impact SCAN mode MS libraries

## ANALYTICAL CHARACTERISTICS OF THE DLLME-GC-MS METHOD

Compound	Linearity ( $\text{ng g}^{-1}$ )	DL ( $\text{ng g}^{-1}$ )	QL ( $\text{ng g}^{-1}$ )
Styrene	4.6-400	1.4	4.6
p-TBP	4.1-400	1.2	4.1
BHA	2.0-400	0.6	2.0
PP	2.0-400	0.6	2.0
TBMP	9.6-400	2.9	9.6
HP	9.9-400	5.1	9.9
DEP	2.0-400	0.6	2.0
TOP	2.0-400	0.6	2.0
OP	2.0-400	0.6	2.0
NP	9.7-400	2.9	9.7
DBP	2.0-400	0.6	2.0
Oleamide	2.0-400	0.6	2.0
BPA	2.0-400	0.6	2.0
BBP	2.0-400	0.6	2.0
DEHP	2.0-400	0.6	2.0

## SAMPLES QUANTIFICATION ( $\text{ng g}^{-1}$ )

Compound	PET 1	PET 2	PET 3	PET 4	PS 1
Styrene	ND	ND	ND	ND	310 $\pm$ 15
p-TBP	35 $\pm$ 1	ND	ND	ND	107 $\pm$ 12
BHA	ND	ND	ND	ND	ND
PP	ND	ND	ND	ND	ND
TBMP	ND	ND	ND	ND	ND
HP	ND	ND	ND	ND	ND
DEP	21 $\pm$ 0.8	17 $\pm$ 0.6	19 $\pm$ 1	ND	ND
TOP	ND	ND	ND	ND	ND
OP	334 $\pm$ 2	ND	ND	ND	ND
NP	15 $\pm$ 0.7	ND	ND	ND	ND
DBP	49 $\pm$ 2	ND	203 $\pm$ 7	65 $\pm$ 5	156 $\pm$ 8
Oleamide	275 $\pm$ 10	115 $\pm$ 8	ND	ND	ND
BPA	250 $\pm$ 11	260 $\pm$ 9	ND	ND	ND
BBP	258 $\pm$ 9	ND	ND	ND	ND
DEHP	18 $\pm$ 0.1	ND	212 $\pm$ 16	ND	250 $\pm$ 17



None of the studied samples exceeded the maximum levels allowed by European legislation

**RECOVERY STUDIES:** The recoveries obtained for the samples at two spiking levels (10 and 100  $\text{ng g}^{-1}$ ) ranged from 82-103%

ND: not detected. <sup>a</sup> Mean  $\pm$  standard deviation (n=3)

**Conclusion:** The DLLME-GC-MS developed method was seen to be a useful approach for the quantification and identification of migrants from plastics in challenging samples such as honey. The method allowed the quantification of fifteen target compounds which were expected to migrate into food and, simultaneously, identified untargeted species (other chemical additives and their degradation products) that also showed a tendency to migrate.

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