Determination of adhesive acrylates in recycled polyethylene terephthalate by fabric phase sorptive extraction coupled to ultra performance liquid chromatography - mass spectrometry

Mahdiyeh Otoukesh[a,b], Cristina Nerín[a]*, Margarita Aznar[a], Abuzar Kabir[c], Kenneth G. Furton[c] , Zarrin Es'haghi[d]

[a]Analytical Chemistry Department, GUIA Group, I3A, EINA, University of Zaragoza, Mª de Luna 3, 50018, Zaragoza, Spain

[b]Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Iran

[c]International Forensic Research Institute, Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, FL, 33199, USA

[d]Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

*Corresponding author.

E-mail address: cnerin@unizar.es

Abstract

This article presents fabric phase sorptive extraction (FPSE) as a simple and effective pre-concentration method for the enrichment of acrylate compounds in different food simulants and subsequent analysis of the extracts by ultra-high-performance liquid chromatography with mass spectrometric detection (UPLC-MS). Acrylate compounds come from acrylic

adhesives used commonly for sticking the paper labels on polyethylene terephthalate (PET) bottles and therefore, they may exist in recycled polyethylene terephthalate (rPET). Four acrylates were studied: ethylene glycol dimethacrylate (EGDM), pentaerythritol triacrylate (PETA), triethylene glycol diacrylate (TEGDA) and trimethylolpropane triacrylate (TMPTA). Five different types of FPSE media coated with different sol-gel sorbents were studied and finally sol-gel polyethylene glycol- polypropylene glycol-polyethylene glycol triblock copolymer (PEG-PPG-PEG) coated FPSE media was chosen for its satisfactory results. The optimal conditions affecting the extraction efficiency of compounds were determined in three different food simulants. Statistical evaluation of this method reveals good linearity and precision. Under the optimized conditions, the method provided limits of detection of the compounds in the range of (0.1-1.9 ng g^{-1}, 0.1- 1.2 ng g^{-1}, 0.2- 2.3 ng g^{-1}) in EtOH 10%, HAc 3% and EtOH 20% and the enrichment factor values (EFs) after applying N_2 were in the range of 11.1- 25.0, 13.8- 26.3, 8.3- 21.9, in simulants A, B and C respectively. The optimized method was applied successfully to analyze thirteen types of recycled PET samples. Acrylates were found in some of the samples at ng g^{-1} levels.

Key words: Fabric phase sorptive extraction (FPSE), Recycled PET, Acrylate adhesives, migration

1. Introduction

Polyethylene terephthalate (PET) is a semi-crystalline thermoplastic polyester polymer with heteroatoms in the backbone. It is non-degradable under normal conditions as it has high molecular weight, a highly hydrophobic nature, high stable C-C and C-H covalent bonds, and no hydrolysable groups [1-5]. PET and its recycled products are primarily used in commercial plastics in the world [6, 7]. In recent years, PET waste has become one of the valuable recyclable materials due to its excellent chemical, physical and mechanical properties, adequate gas barrier and good recyclability, low diffusivity, high inertness and transparency. Recycled PET (rPET) is utilized widespread in the manufacture of different products such as: food packaging, textile fibers, filaments, trays for food contact and beverage bottles, etc.

53 [1, 2, 6-9]. It is estimated that millions of tons of PET are recycled each year. There
54 are different methods used for recycling PET such as depolymerizing to oligomers,
55 melting, incineration, and mechanical processes, but most of rPET is nowadays
56 produced by mechanical recycling [6]. Any production process of recycled material for
57 food contact application must be previously evaluated by EFSA, as it is stated in Regulation
58 282/2008 [10]. When rPET is used for food contact instead of virgin PET, a higher
59 quantity of non intentionally added substances (NIAS) can be expected, since not
60 only the initial additives used for PET manufacturing or the presence of oligomers
61 [8] must be taken into account but also the presence of contaminants coming from
62 the recycling process. These contaminants can have different origins such as the inks
63 or adhesives present in the packaging, degradation processes or the use of recycling
64 stabilizers. Different kind of contaminants have been found such as toluene,
65 benzophenone, tetracosane, benzene and chloroform [11, 12], phthalates [13] as well
66 as residues from adhesives, etc. Components coming from adhesives include a high
67 variety of substances such as antioxidants, polymers, adhesion promoters, solvents,
68 tackifiers, fillers, plasticizers, etc. [14-16].

69 Acrylic polymers, copolymers or terpolymers are commonly applied as dispersions,
70 emulsions or water-soluble adhesives and glue in manufacturing of different films
71 and laminates [17-19] or used for attaching paper labels on PET. The removal of
72 adhesives from PET is necessary to produce a good quality of rPET. However, this
73 task is difficult and often an unknown proportion of adhesives remain in the
74 postconsumer PET. The amount of adhesive is usually expressed by weight,
75 including PET flakes where the adhesive cannot be removed, and no specific
76 analysis is provided. Then, the compounds remain in the final material and can be
77 degraded under the high temperature applied during the recycling process and
78 manufacture of the final food packaging.

79 As any kind of food contact material, rPET must fulfill the Regulation (EC)
80 1935/2004 which means that its constituents should not be transferred to the food in
81 contact at levels that could: (i) health risk for human; (ii) bring about an
82 unacceptable change in the composition of the food; or (iii) bring about deterioration

83 in the organoleptic characteristics thereof [20]. In addition, since rPET is a plastic
84 material it must fulfill Regulation EU/10/2011, that contains a list of authorized
85 substances for production of plastic food contact materials with different specific
86 migration limits (SML) [21]. However, the non-listed compounds migrating from
87 food contact materials cannot surpass the 10 µg/Kg food. Most of the residues from
88 adhesives are in this group.

89 There are a few scientific publications dealing with the potential migration of
90 adhesives constituents and particularly acrylate adhesives [16, 17, 22-29] but none of
91 them studied the migration from rPET. In fact, as far as we know, the analysis of
92 adhesives in postconsumer PET has never been tackled. For this reason, there is a
93 need to develop a method with low detection limits and a good selectivity to pre-
94 concentrate and determine acrylate adhesive residues in rPET and in food simulants.

95 There are several sample preparation techniques such as liquid–phase extraction [30,
96 31], solid phase extraction [32], solid phase microextraction (SPME) [11, 33] and
97 fabric phase sorptive extraction (FPSE) that can be used for the concentration and
98 extraction of compounds from liquid samples.

99 FPSE was first developed by Kabir and Furton in 2013 [34, 35] as a new generation
100 of sorptive microextraction technique. This method efficiently overcomes the
101 shortcoming related to conventional sorbent based sample preparation techniques.
102 FPSE has been fabricated by flexible and permeable natural or synthetic fabric
103 substrates such as cellulose cotton and polyester, where a porous hybrid organic–
104 inorganic sorbent with unique selectivity and affinity towards the target analytes, is
105 chemically immobilized through the sol-gel coating technology on it. Because of its
106 high surface area, high loading of sol-gel coating resulting high sample capacity,
107 high enrichment factor and minimal solvent consumption, among other advantages
108 [36-38], FPSE has been the selected technique for this study.

109 In the present study, FPSE was proposed as an effective method for pre-
110 concentration and extraction of acrylate compounds migrates from recycled PET.
111 During the experiments, three food simulants were tested in order to mimic the mass

112 transfer to food in contact with the packaging: simulant A (ethanol 10%), simulant B
113 (acetic acid 3%) and simulant C (ethanol 20%) [39, 40]. The analysis of extracted
114 compounds was done by ultra-high-performance liquid chromatography UPLC-MS-
115 MS (QqQ). Parameters such as extraction time, desorption solvent, pH and ionic
116 strength were optimized. Quantitative results as well as recovery and reproducibility
117 were obtained.

118 **2. Materials and methods**

119 **2.1. Reagents and FPSE media**

120 Acrylic acid (AA), ethylene glycol dimethacrylate (EGDM), 2-hydroxyethyl
121 methacrylate (HEM), pentaerythritol triacrylate (PETA), triethylene glycol diacrylate
122 (TEGDA) and trimethylolpropane triacrylate (TMPTA) were of analytical quality and
123 purchased from Sigma Aldrich (USA). Chemical structure and physico-chemical properties
124 of these compounds are provided in supplementary material 1. Methanol and acetonitrile for
125 UPLC analysis (LC-MS quality) were purchased from Scharlau Chemie S.A (Sentmenat,
126 Spain). Sodium Chloride (purity: 99.5%) and ethanol (HPLC grade) were purchased from
127 Scharlau Chemie S.A (Sentmenat, Spain), acetic acid (purity>99.8%) from Fluka
128 (Germany) and formic acid (purity>98%) from Sigma- Aldrich Química S.A. (Madrid,
129 Spain). Ultrapure water was obtained from a Wasserlab purification system
130 (QUGR0011; Navarra, Spain).

131 Individual stock solutions of 1500 μg g^{-1} were prepared in ethanol and stored in the dark
132 at 4˚C. The solutions used for the optimization and further experiments were prepared
133 daily in order to avoid potential degradation processes or losses of the analytes.

134 For fabric phase sorptive extraction (FPSE) method development, 5 FPSE media coated with
135 different sol-gel based sorbents characterized with different polarities and selectivities were
136 tested: sol-gel Carbowax 20M (sol-gel CW20M), sol-gel dimethylsiloxane-ethylene oxide
137 block copolymer (sol-gel DBE-C25), sol-gel Chitosan, sol-gel polycaprolactone diol (sol-gel
138 PCL diol) and sol-gel polyethylene glycol-polypropylene glycol-polyethylene glycol triblock
139 copolymer) (sol-gel PEG-PPG-PEG).

140

141 **2.2. Creation of sol-gel sorbent coated fabric phase sorptive extraction media**

142 Creation of fabric phase sorptive extraction media involves a number of distinct and
143 sequential steps: (a) selection and preparation of the fabric substrate; (b) design and
144 preparation of sol solution for sol-gel sorbent coating; (c) creation of sol-gel sorbent
145 coating, chemically bonded to the fabric substrate; (d) conditioning and cleaning of
146 sol-gel sorbent coated fabric phase sorptive extraction media; and (e) slicing the
147 FPSE media into appropriate size. The detailed description of these steps can be
148 found elsewhere [36]. The dimensions of fabrics used in this project were 2.5 cm× 2
149 cm. The molar ration between the sol-gel precursor, methyl trimethoxysilane
150 (MTMS), organic/inorganic polymer, solvent 1 (acetone), solvent 2 (methylene
151 chloride), sol-gel acid catalyst trifluoroacetic acid (TFA), and water were maintained
152 at 1: 7.1x 10^{-3}: 2.01: 2.30: 0.75: 3 for sol-gel CW 20M, 1:0.04:2.01:2.34:0.75:3 for
153 sol-gel DBE-C25, 1:0.25:2.01:2.34:0.75:3 for sol-gel PCL diol,
154 1:0.13:2.01:2.34:0.75:3 for sol-gel PEG-PPG-PEG. The molar ratio of MTMS:
155 Chitosan: glycerin: methanol: water: TFA was maintained at 1: 1.2 x10^{-4} : 0.65 : 7.4 :
156 3.3: 0.30 for sol-gel Chitosan.

157

158 **2.3. UPLC-MS(QqQ) analysis**

159 Ultra-performance liquid chromatography mass spectrometry detection equipped with
160 triple quadrupole mass analyzer [UPLC-MS (QqQ)] in an Acquity system supplied by
161 Waters (Milford; MA, USA) was used. The column was a UPLC BEH C18 of 1.7 µm
162 particle size and the dimension of 2.1 × 100 mm from Waters.

163 The UPLC system was connected with an electrospray (ESI) probe to the triple
164 quadrupole mass analyzer supplied by Waters (TQ Detector, Acquity™ Ultra
165 Performance LC, Milford; MA, USA). The ESI probe was used in positive and negative
166 mode. Acquisitions were carried out in SIR (selected ion recording) mode as there were no
167 matrix interferences at the retention time of the analytes. Table 1 shows the ions monitored

168 and cone voltages used for ionization of each analyte. The mass parameters were
169 optimized by infusing 5 mg L^{-1} of individual standard solutions of each compound in the
170 UPLC-MS (QqQ) system at 10 µLmin^{-1}. The chromatographic conditions used for
171 quantification are described in Table 2.

172

173 **2.4. Sample preparation**

174 Thirteen different kinds of postconsumer flakes and pellet samples of recycled
175 polyethylene terephthalate (rPET) were obtained from several companies. Samples 01
176 and 02 were flakes and samples from 03 to 13 were pelletized rPET. In order to increase
177 their contact surface area and homogeneity, the rPET pellet samples were cryogenically
178 milled to powder using liquid nitrogen. The flakes samples were used without any
179 pretreatment.

180 Migration was evaluated under accelerated conditions in the rPET samples. An amount
181 of 10.0 g of samples were weighted and transferred to a 100-mL glass container and then
182 50 mL of the simulant were added (A: ethanol 10%, B: acetic acid 3% and C: ethanol
183 20%). Then, the glass containers were shaken in order to guarantee a deep contact
184 between the simulant and the sample. The glass containers were closed and kept in an
185 oven at 70 °C for 2 h. After this time, the samples were left to cool down at room
186 temperature. Subsequently, the supernatants were collected, filtered through the 0.22 µm
187 Nylon filter, and transferred to glass containers and used for further experiments. Three
188 replicates of each sample were analyzed.

189 **2.5. Fabric phase sorptive extraction procedure**

190 In order to do the FPSE sample extraction the following steps were followed:

191 ***I. FPSE media cleaning step:*** FPSE media were placed in a vial with 5 mL of a
192 mixture of methanol/acetonitrile (50:50 v/v) and ultrasonicated for 30 min.
193 Subsequently, the FPSE media were removed, rinsed with deionized water and dried
194 in the air [36].

195 ***II. Sample preconcentration step:*** 10 ml of liquid simulant sample were added into
196 the 20-mL screw-capped glass vials containing a magnetic stir bar and FPSE media,
197 and stirring at 900 rpm for 40 min with a Digital magnetic hotplate stirrer from IKA
198 (RT 10; Staufen, Germany). Then, the solution was removed and 1 mL of methanol
199 was added to FPSE media for the back extraction step. The vial was placed in an
200 ultrasonic bath 40 kHz from Branson (3510; Dietzenbach, Germany) for 10 min for
201 back extraction. Afterwards, the FPSE media was removed, and the extract was
202 filtered and analyzed by UPLC-MS (QqQ). Three replicates of each sample and also
203 blank sample consisting of pure simulants were analyzed.

204 ***III. Concentration of the extract***

205 In order to increase the concentration of analytes, the extract was concentrated to dryness
206 under a nitrogen current and then re-dissolved in 50 µL of methanol. The final extracts
207 were analyzed by UPLC-MS (QqQ)

208

209 **2.6. Determination of enrichment factor and extraction recovery**

210 Enrichment factor (EF) and extraction recoveries (ER %) were employed to evaluate the
211 extraction efficiency. EF was calculated before and after concentrating the extract with
212 nitrogen.

213 The enrichment factors (EFs) for all the compounds were calculated according to the
214 following equation:

215 $$EF = \frac{C_{final}}{C_{initial}}$$

216 where C_{final} is the concentration of the analyte in the desorption solvent, and $C_{initial}$ is the
217 initial concentration of analyte in the sample solution.

218 The percentage of extraction recovery (ER%) for the proposed method was calculated
219 according to the following equation:

220 ER%= $\frac{g_{final}}{g_{initial}} \times 100 = EF \times \frac{g_o}{g_s} \times 100$

221 where g_s is the sample weight, g_o is the organic solvent weight, and $g_{initial}$ and g_{final} are
222 the number of grams of the analyte present in the sample solution and the number of
223 grams of the analyte finally collected in the organic solvent, respectively [41]

224 **3. Results and discussion**

225 For the optimization process, solutions at a concentration of 100 ng g^{-1} of each
226 compound were prepared in three different food simulants: simulant A (ethanol 10%),
227 simulant B (acetic acid 3%) and simulant C (ethanol 20%), just before performing the
228 experiments, except for the selection of the FPSE media where water was used at 2
229 different concentration levels, 50 and 100 ng g^{-1}. Different parameters were optimized
230 in order to maximize the extraction efficiency. The optimization parameters include:
231 selection of the fabric phase media, extraction time, kind of back extraction solvent,
232 pH of the solution and the effect of ionic strength.

233 **3.1. Optimization of the FPSE methodology**

234 **3.1.1. Selection of the FPSE media**

235 Five different FPSE media coated with polymers of different polarities such as: sol- gel
236 CW20M, sol-gel DBE-C25, sol-gel Chitosan, sol-gel PCL diol, and sol-gel PEG-PPG-
237 PEG, were evaluated in aqueous solutions for the target analytes. Initial solutions were
238 prepared in water at 2 concentration levels, 50 ng g^{-1} and 100 ng g^{-1} in order to observe
239 the extraction efficiency in a wide range of concentration. Testing conditions were as
240 follows: 10 mL of sample volume, 30 min of extraction time and 1 mL of methanol as
241 desorption solvent and 10 min as desorption time. The results shown in Fig. 1 indicate
242 that the best extractions were provided by sol-gel PEG-PPG-PEG for all the tested
243 compounds. Similar results were found at the 2 sample concentration levels. According
244 to these results, FPSE was not efficient for acrylic acid (AA) and 2-hydroxyethyl
245 methacrylate (HEM) as the enrichment factor for these two compounds was below 1 in
246 all media, so these compounds were removed from the experiment. It is worthy to

247 mention that both AA and HEM are strongly polar and weak organic acids. As such,
248 they remain partially in ionized state in water and require either matrix pH adjustment
249 or mixed mode sorbent chemistry for their effective extraction and preconcentration.

250 **3.1.2. Effect of the desorption solvent**

251 After the extraction, the compounds previously retained in the FPSE media must be eluted
252 with a suitable desorption solvent and subsequently analyzed by the UPLC-MS (QqQ).
253 Two different organic solvents, methanol and acetonitrile, were tested as back extraction
254 solvents. Methanol was selected as the best one since it provided an elution ability
255 slightly higher than acetonitrile (Supplementary material 2).

256 **3.1.3. Effect of extraction time**

257 The extraction equilibrium time is an important parameter in the optimization process in
258 order to reach the extraction equilibrium. A series of extraction times ranging from 10 to
259 60 min was examined, and the results are shown in Fig. 2a, b and c for each simulant. It
260 was found that the highest sorption of the analytes was almost reached when the
261 extraction time was 40 min and after that, the equilibrium was reached in all situations.
262 The results also showed that the extraction pattern was similar for all simulants. Only in
263 ethanol 20% TEGDA and EGDM did not seem to increase their extraction with time. So,
264 an optimum extraction time of 40 min was accepted for subsequent experiments.

265 **3.1.4. Effect of salt addition**

266 The effect of salt addition is presented in supplementary material 3. The figures shows
267 the effect of adding different concentrations of sodium chloride (0, 5, 10, 15% w/v) on
268 the adsorption of the evaluated analytes on the fabric. Similar adsorption of the analytes
269 from simulant A and C (ethanol 10% and ethanol 20%) was found: adsorption increased
270 with the increase of NaCl concentration from 0 to 5%, and then it decreased with further
271 increase of NaCl concentration. In simulant B (acetic acid 3%) the increase was observed
272 when 10% of NaCl was added. These variations with NaCl concentration in the
273 extraction can be explained by the fact that the addition of salt to a sample solution can
274 present two contradictory effects. On one hand, there is an increase of the ionic strength

275 and a salting-out effect, reducing the solubility of the analyte in the aqueous solution and
276 then facilitating the availability of the target analyte in the sorption media. On the other
277 hand, at high NaCl concentrations, there can be an increase of viscosity that negatively
278 affects mass transfer of analytes and consequently, the sorption of the compounds by the
279 FPSE media. Therefore, 5% NaCl was chosen for simulant A and C and 10% of salt was
280 chosen for simulant B.

281 **3.1.5. Effect of pH**

282 The effect of pH on the extraction of acrylates was studied at three levels; acidic
283 (pH=2.25 in simulant B), almost neutral (pH=5.44 in deionized water) and basic
284 (pH=9.92 by adding 0.1M NaOH solution to the deionized water). The results showed
285 that there were no appreciable changes in the extraction efficiency of the analytes at the
286 different pH levels. Therefore, no pH adjustment was done in the subsequent
287 experiments.

288

289 **3.2. Analytical performance characteristics of the method**

290 The analytical parameters were evaluated under the optimum experimental conditions
291 in three simulants and in terms of linearity, repeatability (expressed as RSD%), limits of
292 detection (LODs), limits of quantification (LOQs) (Table 3). Calibration curves were
293 constructed in each simulant by plotting the peak area against the sample concentration.
294 There was excellent linearity, with good coefficient of determination (R^2) for the target
295 analytes in all the simulants. LODs and LOQs of the method were calculated for each
296 individual peak on the basis of a signal-to-noise (S/N) ratio of 3 and 10, respectively.
297 Very low detection limits were obtained for all the compounds and simulants, with
298 values in the range from 0.1 to 2.3 ng g^{-1}. The repeatability was studied for 3 replicate
299 analyses of the samples in a middle point of the linear range, at 100 ng g^{-1}, and under
300 aforementioned optimized conditions. The relative standard deviations (RSD%) for the
301 detected compounds ranged from 1.5% to 7.0%, indicating good precision of the method.
302 The extraction recovery (ER %) and EF were calculated using the equations and method
303 mentioned in section 2.6 and the results are presented in Table 4. The best EF values

304 were achieved for acetic acid 3% and ethanol 10% rather than ethanol 20%, probably
305 because this simulant has a higher hydrophobic nature and the target analytes have a
306 higher tendency to remain in it.

307 The chromatograms obtained for the target analytes at 12 ng. g $^{-1}$ and analyzed by FPSE
308 following UPLC-MS are shown in Supplementary material 4.

309

310 **3.3 Real sample analysis**

311 The extracts coming from the migration condition were analyzed by FPSE method
312 followed by UPLC/MS, to determine the acrylates concentration in rPET samples when
313 they were in contact with 3 kinds of food simulants. Sample preparation was carried out
314 according to section 2.4. The migration results showed that most of the target analytes in
315 the samples had concentration values below the limit of detection of the method and also
316 below 10 ng g $^{-1}$ (Table 5).

317 Previous works have reported the presence of acrylates in acrylic adhesives used in food
318 packaging. Canellas has determined the main volatile and non-volatile compounds
319 present in different acrylic adhesives as well as their partition and diffusion coefficients
320 and its migration to Tenax as food simulant [26] [16] [28]. Two acrylates were identified
321 by gas chromatography in several adhesives, butyl acrylate and 2-ethylhexyl acrylate but
322 their values in migration were always below the SML established in EU/10/2011
323 regulation (no SML and 0.05 mg Kg $^{-1}$ respectively). When the analysis was performed
324 by liquid chromatography and high resolution mass spectrometry, 2-(2-(2-
325 methoxyethoxy) ethoxy)ethyl methacrylate was proposed as a candidate in adhesives
326 composition.

327 In the study performed by Franz and Brandsch regarding modelling migration of
328 acrylic monomers from methacrylate polymers to saliva, water, Miglyol 840 and Tenax.
329 [29] it was shown that acrylic polymer materials used for rigid plastics applications

330 exhibited an extremely low diffusion behavior that therefore low migration values would
331 be expected.

332 To study the interaction of these compounds in rPET, 10g of each rPET sample (in
333 powder form) were spiked with 1 mL of the analytes solution (5 μg g^{-1}), being 5000 ng
334 the final quantity of analytes added. Then, it was left at room temperature for 24 hours.
335 Then, the samples were immersed in 50 mL of the three simulants at 70ºC for 2 hours.
336 Finally, an aliquot of 10 mL from each simulant was extracted by FPSE following the
337 protocol described in section 2.5, not using concentration under nitrogen. This study was
338 done by triplicate. Fig. 3 shows the quantity (ng) of each acrylate found in the 3
339 simulants after being in contact with the spiked rPET. As can be seen, EGDM and
340 TEGDA, with a more linear chemical structure derived from ethylene glycol, had a
341 higher interaction with rPET, than TMPTA and PETA. The same pattern was observed
342 for the three simulants. Thus, it could be expected that the migration of EGDM and
343 TEGDA from rPET to food simulants were lower than that of TMPTA and PETA.

344

345 **4. Conclusion**

346 In this study, FPSE combined to UPLC-MS (QqQ) was applied to the determination
347 of migration behavior of residual components from acrylate adhesives from thirteen
348 samples of rPET supplied by several EU companies. Five different polar FPSE
349 media were investigated and PEG-PPG-PEG was chosen as the best one. FPSE
350 provided satisfactory results with good linear range and detection limits in the range
351 of 0.1 to 2.3 ng/g. This method has demonstrated high enrichment factor with
352 unique advantages including simplicity, fast extraction, and low consumption of
353 solvent.

354

355 **Acknowledgements**

356 The authors would like to acknowledge Projects AGL2015-67362-P from MINECO (Spain)
357 and the Aragon Government and European Social Funds for the financial help given to GUIA
358 groupT53_17R.

359

360 **References**

361 [1] R. Shamsi, M. Abdouss, G.M.M. Sadeghi, F.A. Taromi, Synthesis and characterization of
362 novel polyurethanes based on aminolysis of poly(ethylene terephthalate) wastes, and
363 evaluation of their thermal and mechanical properties, Polymer International, 58 (2009) 22-
364 30.
365 [2] N. Torres, J.J. Robin, B. Boutevin, Study of thermal and mechanical properties of virgin
366 and recycled poly(ethylene terephthalate) before and after injection molding, European
367 Polymer Journal, 36 (2000) 2075-2080.
368 [3] H. Webb, D. Lemire, O. Kaser, Diamond dicing, Data & Knowledge Engineering, 86
369 (2013) 1-18.
370 [4] R. Gautam, A.S. Bassi, E.K. Yanful, A review of biodegradation of synthetic plastic and
371 foams, Applied Biochemistry and Biotechnology, 141 (2007) 85-108.
372 [5] J. Yang, Y. Yang, W.-M. Wu, J. Zhao, L. Jiang, Evidence of Polyethylene Biodegradation
373 by Bacterial Strains from the Guts of Plastic-Eating Waxworms, Environmental Science &
374 Technology, 48 (2014) 13776-13784.
375 [6] L. Gouissem, A. Douibi, D. Benachour, The evolution of properties of recycled
376 poly(ethylene terephthalate) as function of chain extenders, the extrusion cycle and heat
377 treatment, Polymer Science Series A, 56 (2014) 844-855.
378 [7] C.C. Lin, Recycling technology of poly(ethylene terephthalate) materials,
379 Macromolecular Symposia, 135 (1998) 129-135.
380 [8] S. Ubeda, M. Aznar, C. Nerín, Determination of oligomers in virgin and recycled
381 polyethylene terephthalate (PET) samples by UPLC-MS-QTOF, Analytical and Bioanalytical
382 Chemistry, 410 (2018) 2377-2384.
383 [9] X. Lin, J. Yu, H. Li, J.Y.K. Lam, K. Shih, I.M.L. Sham, C.K.Y. Leung, Recycling
384 polyethylene terephthalate wastes as short fibers in Strain-Hardening Cementitious
385 Composites (SHCC), Journal of Hazardous Materials, 357 (2018) 40-52.
386 [10] Commission regulation(EC) No 282/2008 of 27 March 2008 on recycled plastic
387 materials and articles intended to come into contact with foods and amending Regulation
388 (EC) No 2023/2006, Official Journal of the European Union, (2008) 9- 18.
389 [11] É.C. Oliveira, Y. Echegoyen, S.A. Cruz, C. Nerin, Comparison between solid phase
390 microextraction (SPME) and hollow fiber liquid phase microextraction (HFLPME) for
391 determination of extractables from post-consumer recycled PET into food simulants, Talanta,
392 127 (2014) 59-67.
393 [12] w.A. Hargraves, D.J. Armstrong, Determination of benzene residues in recycled
394 polyethylene terephthalate (PETE) by dynamic headspace-gas chromatography AU -
395 komolprasert, Vanee, Food Additives & Contaminants, 11 (1994) 605-614.

396 [13] S. Keresztes, E. Tatár, Z. Czégény, G. Záray, V.G. Mihucz, Study on the leaching of
397 phthalates from polyethylene terephthalate bottles into mineral water, Science of The Total
398 Environment, 458-460 (2013) 451-458.
399 [14] E.M. Petrie, Handbook of Adhesives and Sealants, Second Edition, The McGraw-Hill
400 Companies, Inc., (2007).
401 [15] G. Gierenz, W. Karmann, Adhesion and Adhesive Tapes, Brisbane; Chichester; New
402 York; Weinheim, Wiley-VCH., (2001).
403 [16] E. Canellas, P. Vera, C. Domeño, P. Alfaro, C. Nerín, Atmospheric pressure gas
404 chromatography coupled to quadrupole-time of flight mass spectrometry as a powerful tool
405 for identification of non intentionally added substances in acrylic adhesives used in food
406 packaging materials, Journal of Chromatography A, 1235 (2012) 141-148.
407 [17] Z.Y. Lee, S.S. Raghavan, F.J. Ghadessy, Y.N. Teo, Rapid and sensitive detection of
408 acrylic acid using a novel fluorescence assay, communication, 4 (2014) 60216–60220.
409 [18] F. Isella, E. Canellas, O. Bosettia, C. Nerinb, Migration of non intentionally added
410 substances from adhesives by UPLC–Q-TOF/MS and the role of EVOH to avoid migration in
411 multilayer packaging materials, journal of mass spectrometry, 48 (2013) 430–437.
412 [19] J. Cohrs, Migration testing of adhesives intended for food contact materials, FEICA, the
413 Association of the European Adhesive & Sealant Industry, (2016).
414 [20] Regulation (EC) No. 1935/2004 of the European Parliament and of the Council on
415 materials and articles intended to come into contact with food and repealing Directives
416 80/590/EEC and 89/109/EEC

417 Official Journal of the European Union L 338, (2004) 4-17.
418 [21] T.E. COMMISSION, Commission Regulation (EU) No 10/2011 of 14 January 2011 on
419 plastic materials and articles intended to come into contact with food, Official Journal of the
420 European Union, (2011).
421 [22] A. Gruner, O. Piringer, Component migration from adhesives used in paper and
422 paperboard packaging for foodstuffs, Packaging Technology and Science, 12 (1999) 19-28.
423 [23] G. Lawson, C.T. Barkby, C. Lawson, Contaminant migration from food packaging
424 laminates used for heat and eat meals, Fresenius' Journal of Analytical Chemistry, 354 (1996)
425 483-489.
426 [24] G. Lawson, S. Bartram, S. Fitchner, E.D. Woodland, MALDI-MS and colorimetric
427 analysis of diisocyanate and polyol migrants from model polyurethane adhesives used in food
428 packaging, Analyst, 125 (2000) 115-118.
429 [25] A. Störmer, R. Franz, MIGRESIVES: a research project on migration from adhesives in
430 food-packaging materials in support of European legislation and standardization, Food
431 Additives & Contaminants: Part A, 26 (2009) 1581-1591.
432 [26] E. Canellas, M. Aznar, C. Nerín, P. Mercea, Partition and diffusion of volatile
433 compounds from acrylic adhesives used for food packaging multilayers manufacturing,
434 Journal of material chemistry, 20 (2010) 5100–5109.
435 [27] M.A. Pemberton, B.S. Lohmann, Risk Assessment of residual monomer migrating from
436 acrylic polymers and causing Allergic Contact Dermatitis during normal handling and use,
437 Regulatory Toxicology and Pharmacology, 69 (2014) 467-475.
438 [28] E. Canellas, P. Vera, C. Nerin, Risk assessment derived from migrants identified in
439 several adhesives commonly used in food contact materials, Food and Chemical Toxicology,
440 75 (2015) 79–87.

441 [29] R. Franz, R. Brandsch, Migration of Acrylic Monomers from Methacrylate Polymers – Establishing Parameters for Migration Modelling, Packaging Technology and Science, 26 (2013) 435-451.
444 [30] S.X.L. Goh, H.K. Lee, An alternative perspective of hollow fiber-mediated extraction: Bundled hollow fiber array-liquid-phase microextraction with sonication-assisted desorption and liquid chromatography–tandem mass spectrometry for determination of estrogens in aqueous matrices, Journal of Chromatography A, 1488 (2017) 26-36.
448 [31] N. Campillo, I. López-García, M. Hernández-Córdoba, P. Viñas, Food and beverage applications of liquid-phase microextraction, TrAC - Trends in Analytical Chemistry, 109 (2018) 116-123.
451 [32] A. Sa'adi, Z. Es'haghi, Azo-phenol ligand surface-active magnetic graphene oxide nanosheets as solid-phase adsorbents for extraction of cadmium in food samples, Journal of Food Measurement and Characterization, (2018).
454 [33] L. Zhang, E. Gionfriddo, V. Acquaro, Jr., J. Pawliszyn, Direct immersion solid-phase microextraction analysis of multi-class contaminants in edible seaweeds by gas chromatography-mass spectrometry, Analytica Chimica Acta, 1031 (2018) 83-97.
457 [34] A. Kabir, K.G. Furton, A. Malik, Innovations in sol-gel microextraction phases for solvent-free sample preparation in analytical chemistry, TrAC Trends in Analytical Chemistry, 45 (2013) 197-218.
460 [35] A. Kabir, K.G. Furton, Fabric phase sorptive extractors (fpse), US Patent No. 9,283,544, in: U.S.P.a.T. Office (Ed.), (2016).
462 [36] M. Aznar, S. Úbeda, C. Nerin, A. Kabir, K.G. Furton, Fabric phase sorptive extraction as a reliable tool for rapid screening and detection of freshness markers in oranges, Journal of Chromatography A, 1500 (2017) 32-42.
465 [37] A. Anthemidis, V. Kazantzi, V. Samanidou, A. Kabir, K.G. Furton, An automated flow injection system for metal determination by flame atomic absorption spectrometry involving on-line fabric disk sorptive extraction technique, Talanta, 156-157 (2016) 64-70.
468 [38] R.B. García-Guerra, S. Montesdeoca-Esponda, Z. Sosa-Ferrera, A. Kabir, K.G. Furton, J.J. Santana-Rodríguez, Rapid monitoring of residual UV-stabilizers in seawater samples from beaches using fabric phase sorptive extraction and UHPLC-MS/MS, Chemosphere, 164 (2016) 201-207.
472 [39] M. Aznar, E. Canellas, C. Nerín, Quantitative determination of 22 primary aromatic amines by cation-exchange solid-phase extraction and liquid chromatography–mass spectrometry, Journal of Chromatography A, 1216 (2009) 5176-5181.
475 [40] M. Aznar, P. Alfaro, C. Nerin, A. Kabir, K.G. Furton, Fabric phase sorptive extraction: An innovative sample preparation approach applied to the analysis of specific migration from food packaging, Analytica Chimica Acta, 936 (2016) 97-107.
478 [41] M. Yang, Y. Gu, X. Wu, X. Xi, X. Yang, W. Zhou, H. Zeng, S. Zhang, R. Lu, H. Gao, J. Li, Rapid analysis of fungicides in tea infusions using ionic liquid immobilized fabric phase sorptive extraction with the assistance of surfactant fungicides analysis using IL-FPSE assisted with surfactant, Food Chemistry, 239 (2018) 797-805.

482

483

484

Figure Captions

485

486 **Fig. 1.** Enrichment factors (EF) obtained for HEM, AA, EGDM, TEGDA, TMPTA and
487 PETA in in water solution using 5 different FPSE media.

488 **Fig. 2.** Effect of extraction time in extraction of acrylates by FPSE in a) simulant A b)
489 simulant B and c) simulant C.

490 **Fig. 3.** Quantity (ng) of the acrylates found in the simulants after being in contact with the
491 rPET spiked with 5000 ng.

Table 1. Compounds analyzed, CAS number, cone voltage (CV) used in mass spectrometry detection, exact mass (m/z) and adduct detected

Name	CAS n°	CV (KV)	m/z	Adduct
Acrylic acid (AA)	79-10-7	30	71.013	$[MH]^-$
Ethylene glycol dimethacrylate (EGDM)	97-90-5	15	199.097	$[MH]^+$
2-hydroxyethyl-methacrylate (HEMA)	868-77-9	15	131.071	$[MH]^+$
Pentaerythritol triacrylate (PETA)	3524-68-3	30	321.095	$[MNa]^+$
Triethylene glycol diacrylate (TEGDA)	1680-21-3	15	259.118	$[MH]^+$
Trimethylolpropane triacrylate (TMPTA)	15625-89-5	30	319.116	$[MNa]^+$

Table 2: Instrumental parameters for the UPLC-MS analyses. Mobile phases: A (methanol and 0.1% formic acid) and B (water and 0.1% formic acid).

UPLC parameters		
Flow rate	0.3 mL min^{-1}	
Column temperature	40 °C	
Injection volume	10 μL	
Gradient timetable		
Time (min)	% A	% B
0	10.0	90.0
1	10.0	90.0
5	100	0.0
8	100	0.0
8.10	10.0	90.0
9	10.0	90.0
Electrospray MS parameters		
Ionization mode	ESI	
Desolvation gas flow	450 L h^{-1}	
Cone gas flow	60 L h^{-1}	
Desolvation gas temperature	450 °C	
Source temperature	120 °C	
Capillary	3.00 kV	
SIR dwell	0.05 s	

Table 3. Figures of merit for analysis of acrylates in 3 different food simulants by FPSE method in LC-MS, limit of detection (LOD), linear dynamic range (LDR), determination coefficient (R^2) and relative standard deviation (RSD).

Analyte	**LOD ($ng\ g^{-1}$)**			**LR ($ng\ g^{-1}$)**			**R^2**			**RSD%* (n=3)**		
	EtOH 10%	HAc 3%	EtOH 20%	EtOH 10%	HAc 3%	EtOH 20%	EtOH 10%	HAc 3%	EtOH 20%	EtOH 10%	HAc 3%	EtOH 20%
EGDM	0.8	0.9	0.7	3.0- 252.8	2.9- 201.8	2.2- 227.4	0.9946	0.9959	0.9970	3.3	6.3	3.7
TEGDA	0.3	0.1	0.5	0.8- 281.6	0.5- 224.8	1.8- 225.5	0.9905	0.9933	0.9984	3.7	6.3	7.0
TMPTA	0.1	0.1	0.2	0.3- 264.5	0.5- 265.8	0.6- 211.8	0.9901	0.9909	0.9938	3.5	4.9	5.2
PETA	1.9	1.2	2.3	6.3- 260.7	4.1- 261.9	7.8- 289.7	0.9945	0.9909	0.9958	1.5	6.1	2.6

*calculated at 100 $ng\ g^{-1}$

Table 4. Enrichment factor (EFs) and the percentage of extraction recovery(ER%) values after fabric phase sorptive extraction in 3 different food simulants: ethanol 10% (EtOH 10%), acetic acid 3% (HAC 3%), ethanol 20% (EtOH 20%). EFs was calculated before (basic font) and after (italics font) concentration under nitrogen. (4 replicates)

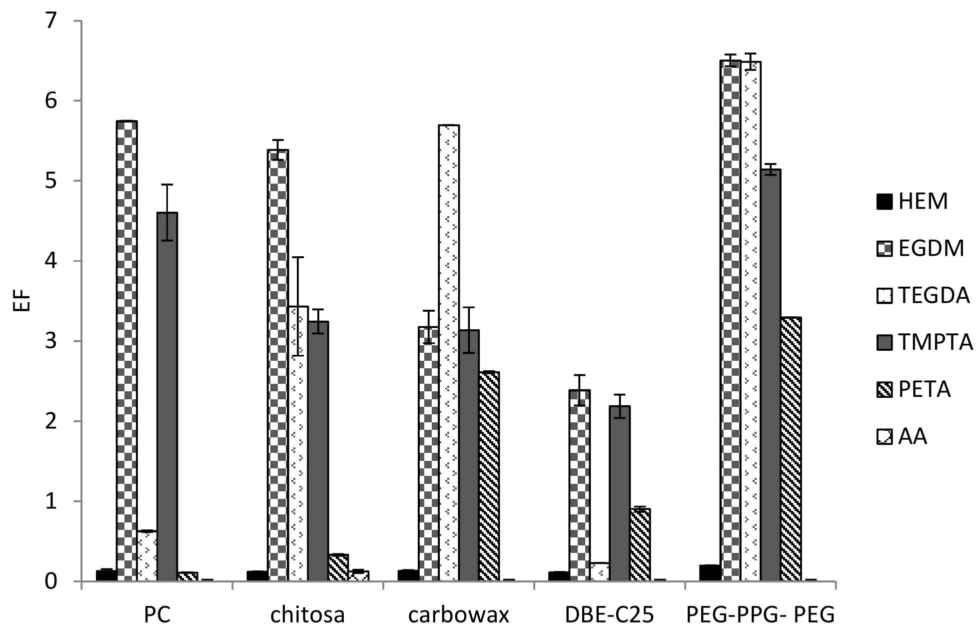
Analyte	**EF[a]**						**ER%[b]**		
	EtOH 10%		HAc 3%		EtOH 20%		EtOH 10%	HAc 3%	EtOH 20%
EGDM	4.0	→*18.8*	4.3	→*20.2*	3.0	→*13.9*	39.9	43.0	29.6
TEGDA	2.1	→*13.5*	3.2	→*21.2*	1.3	→*8.3*	20.6	32.5	12.7
TMPTA	3.1	→*25.0*	3.3	→*26.3*	2.7	→*21.9*	31.2	32.9	27.3
PETA	1.2	→*11.1*	1.5	→*13.8*	1.7	→*16.1*	11.9	14.7	17.2

a Average enrichment factor (C = 50, 100, 150 ng g^{-1}).
b Average extraction recovery(C = 50, 100, 150 ng g^{-1}).

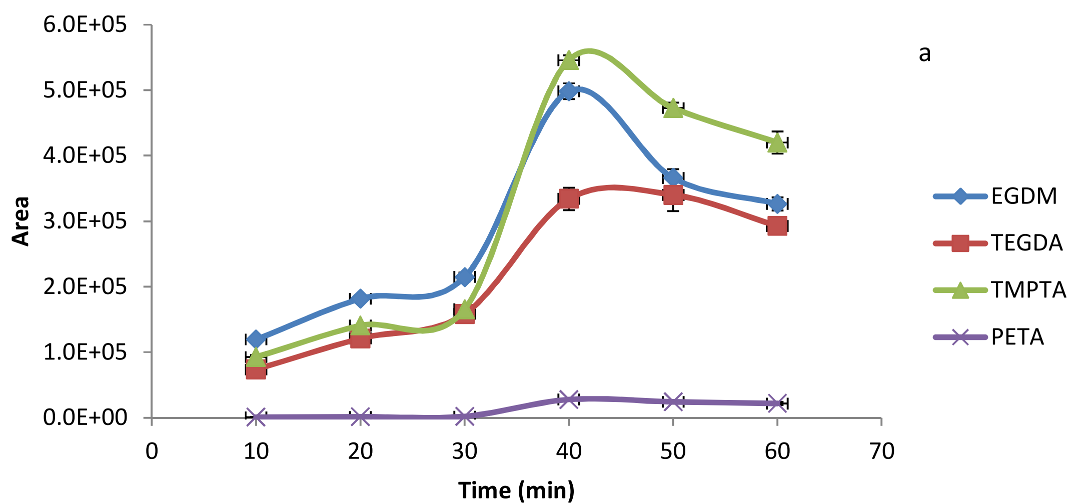
Table 5. Concentration of acrylates (ng g^{-1} simulant) in 3 different simulants, acetic acid 3% (HAc 3%), ethanol 10% (EtOH 10%) and ethanol 20 % (EtOH 20%).

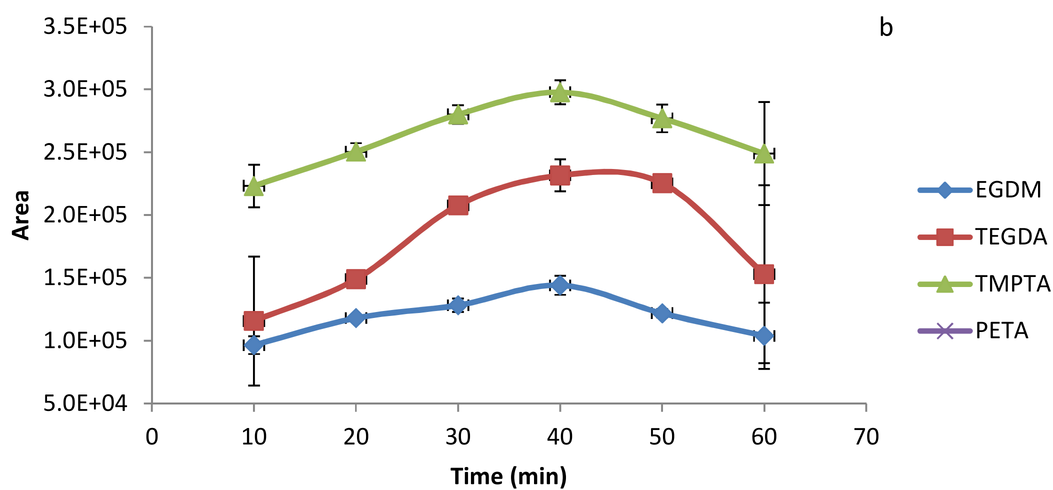
	EGDM (ng g^{-1})			**TEGDA (ng g^{-1})**			**TMPTA (ng g^{-1})**			**PETA (ng g^{-1})**		
	EtOH 10%	**HAc 3%**	**EtOH 20%**	**EtOH 10%**	**HAc 3%**	**EtOH 20%**	**EtOH 10%**	**HAc 3%**	**EtOH 20%**	**EtOH 10%**	**HAc 3%**	**EtOH 20%**
S1	0.437 ± 0.010	0.194 ± 0.002	<LOQ	<LOQ	<LOD	<LOQ	<LOD	0.358 ± 0.006	<LOD	<LOD	<LOD	<LOD
S2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.603 ± 0.067	0.354 ± 0.002	0.641 ± 0.006	<LOD	<LOD	<LOD
S3	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S4	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S5	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S6	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S7	0.433 ± 0.006	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
S8	0.355 ± 0.002	<LOD	<LOD	<LOQ	<LOD	<LOD	0.290 ± 0.006	<LOD	<LOD	<LOD	<LOD	<LOD
S9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD
S10	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD
S11	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ
S12	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	0.272 ± 0.004	<LOQ	<LOD	<LOD	<LOD
S13	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	<LOD

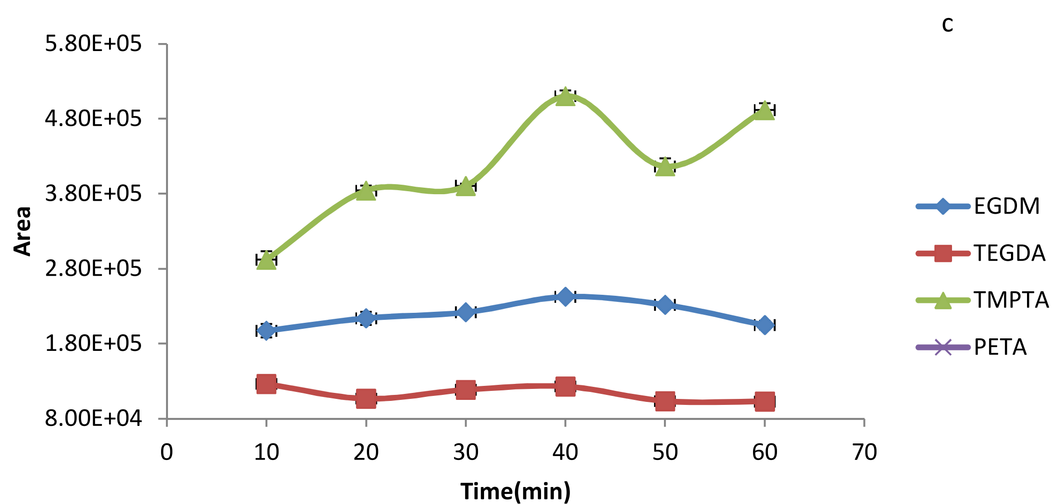
LOD: limit of detection; LOQ: limit of quantification

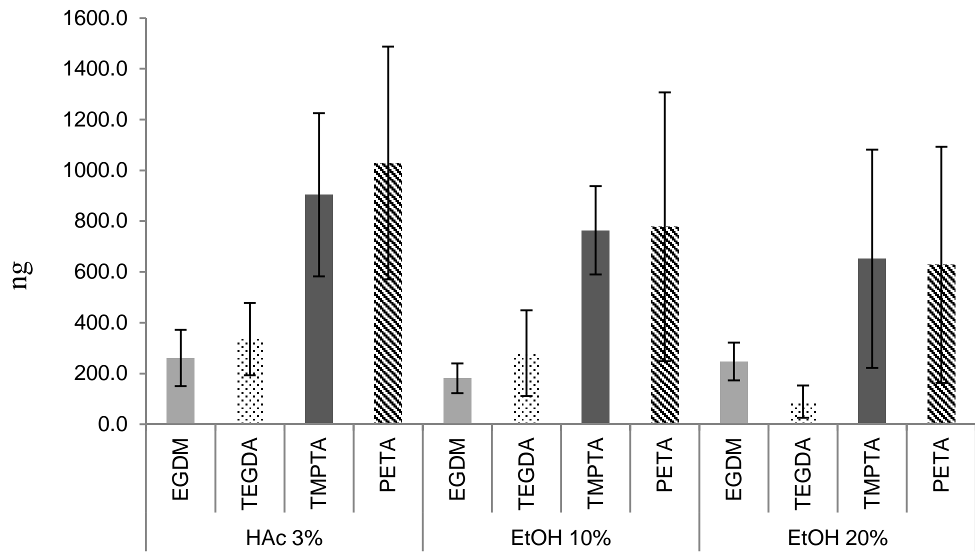


7
6
5
4
3
2
1
0
EF
PC
chitosa
carbowax
DBE-C25
PEG-PPG- PEG
HEM
EGDM
TEGDA
TMPTA
PETA
AA


a
Area
6.0E+05
5.0E+05
4.0E+05
3.0E+05
2.0E+05
1.0E+05
0.0E+00
0
10
20
30
40
50
60
70
Time (min)
EGDM
TEGDA
TMPTA
PETA


b
Area
3.5E+05
3.0E+05
2.5E+05
2.0E+05
1.5E+05
1.0E+05
5.0E+04
0
10
20
30
40
50
60
70
Time (min)
EGDM
TEGDA
TMPTA
PETA


c
Area
5.80E+05
4.80E+05
3.80E+05
2.80E+05
1.80E+05
8.00E+04
0
10
20
30
40
50
60
70
Time(min)
EGDM
TEGDA
TMPTA
PETA



1600.0
1400.0
1200.0
1000.0
800.0
600.0
400.0
200.0
0.0
ng
EGDM
TEGDA
TMPTA
PETA
EGDM
TEGDA
TMPTA
PETA
EGDM
TEGDA
TMPTA
PETA
HAc 3%
EtOH 10%
EtOH 20%