

1 **Non-target screening of organic contaminants in marine salts by gas**
2 **chromatography coupled to high-resolution time-of-flight mass**
3 **spectrometry**

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24 **Abstract**

25 Gas chromatography coupled to time-of-flight mass spectrometry (GC-TOF MS) has
26 been applied to characterize the organic pollution pattern of marine salt samples
27 collected in saltworks from the Spanish Mediterranean coast. After dissolving the
28 samples in water, a solid-phase extraction was applied reaching with a 250-
29 preconcentration factor. The screening methodology allowed the detection of sample
30 components without any kind of pre-selection of target pollutants. The identity of
31 components detected was established by accurate mass measurements and comparison
32 of experimental full-acquisition spectra with theoretical MS libraries. Several organic
33 pollutants were identified in the samples, like plasticizers -potentially toxic to humans-
34 and fragrances -included within the group of pharmaceuticals and personal care
35 products-, among others. Our results indicate that these contaminants can be found in
36 the marine salt after the crystallization process. GC-TOF MS is a powerful technique
37 for wide-scope screening of (semi)volatile, low-polar organic contaminants, able to
38 investigate the presence of a large number of compounds. Searching of contaminants is
39 not restricted to a target list of compounds. Therefore, unexpected contaminants can be
40 discovered in an efficient way, with better sensitivity and selectivity than other
41 conventional analytical techniques, and making use of the powerful qualitative
42 information provided by full-spectrum acquisition at accurate mass.

43

44 **Keywords:** marine salt, saltworks, gas chromatography, mass spectrometry, non-target
45 screening, organic contaminants.

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49 **1. Introduction**

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51 Marine salt is obtained by evaporation of sea water due to the combined effect of wind
52 blow and sunlight heat in the solar saltworks. Saltpans are located near the sea,
53 becoming peculiar environments inhabited by wildlife species associated with high
54 salinity conditions. Concern has arisen as consequence of the vulnerability of these
55 environments to anthropogenic pollution. Run-off from farms and industries may
56 contain high concentrations of pesticides and industrial sub-products and reach these
57 vulnerable coastal locations, with a deleterious impact on the briny aquatic systems [1].
58 This fact can also affect to the quality of the marine salt produced. Several authors have
59 reported the presence of contaminants in coastal sea and saline waters, such as
60 pesticides [2], halocarbons, aliphatic and aromatic hydrocarbons and ketones [3].
61 Badoil and Benanou et al. [4] have detected phenols, phosphates and other volatile and
62 semi-volatile compounds in waste landfill leachates, which reach coastal waters.

63 Contaminants produced by anthropogenic activities are transported by rivers and
64 water flows from wastewater treatment plants and are frequently deposited on coastal
65 locations like salt marshes or river estuaries and deltas. Several authors have detected a
66 variety of contaminants in these vulnerable areas [5, 6]. The marine salts obtained from
67 saltpans can contain the contaminants present in sea water, provided that they remain
68 after the concentration and crystallisation processes. As a consequence, monitoring the
69 presence of organic contaminants in marine salts seems necessary to have a realistic
70 knowledge of their quality, since they are widely used for feeding purposes in human
71 and animal nutrition and also for aquaculture activities, such as the artemia growth.
72 Bath salts could also constitute possible routes of human exposure to the potentially
73 toxic compounds found in the sea salts.

74 Hyphenation of gas chromatography (GC) with mass spectrometry (MS) is the
75 most widely used and accepted technique for determination of volatile and semivolatile
76 compounds of low-medium polarity in aquatic ecosystems, particularly in surface
77 coastal water and marine environments. Different MS analyzers have been applied for
78 this purpose, from single quadrupole to ion-trap or triple quadrupole, although the two
79 later allow working under tandem MS mode [2, 3, 7, 8]. Recently, Silva et al. [3]
80 reported a methodology based on head space solid phase microextraction and GC-
81 quadrupole mass spectrometry for the analysis of volatile compounds in marine salt,
82 able to detect 40 volatile compounds belonging to different chemical groups.

83 The wide majority of methods reported until now in the environmental field are
84 focused on a limited list of target contaminants. Even in the case that target pollutants
85 investigated belong to priority lists, target methods do not allow the wide-scope
86 screening required to investigate a large number of compounds that might be present in
87 the samples. In most target methods, other non-selected contaminants would not be
88 detected due to the specific-analyte information acquired. Although conventional MS
89 analyzers can also work under scan mode, their capability to detect organic
90 contaminants at low levels in complex-matrix samples is rather limited due to their low
91 sensitivity and selectivity and their nominal mass measurements.

92 The recent emergence of modern high-resolution time-of-flight (TOF) analyzers
93 opens new perspectives to develop wide-scope screening methodologies. GC-TOF MS
94 offers interesting features for this purpose, as it combines high full-spectrum sensitivity
95 and elevated mass resolution making feasible the accurate mass measurements of the
96 molecular and/or fragments ions of any GC-amenable compound present in the sample.
97 This technique allows searching organic contaminants in a post-target (i.e. searching for
98 selected compounds after MS acquisition) and also in a non-target way (i.e. searching

99 for unknowns, without any kind of compound pre-selection) [9]. GC-TOF MS has been
100 successfully applied for screening, identification and elucidation of organic pollutants in
101 environmental water and biological samples [9, 10], and also for confirmation of
102 pollutants in highly complex matrix like wastewater [11].

103 The limited dynamic range of GC-TOF MS instruments reduces their potential for
104 quantitative analysis. For this reason, in the present study, GC-TOF MS has been used
105 for qualitative purposes because of its high sensitivity in full spectrum acquisition
106 complemented with mass accuracy.

107 In this work, we have applied GC-TOF MS for the rapid and wide-scope
108 screening of organic pollutants in sea water and in marine salts obtained from solar
109 saltworks and from a pristine sea shore salt marsh sited along the Spanish Western
110 Mediterranean coast. The identity of the sample components detected in a non-target
111 way was established by means of exact mass measurements and by comparison with
112 theoretical spectral libraries. In addition, the organophosphate esters (OPEs) identified
113 were confirmed by injecting reference standards.

114

115 **2. Material and methods**

116 2.1. Sampling points.

117 Marine salt samples from four solar saltworks sited in the Spanish Mediterranean shore
118 (see **Figure 1**) were collected directly from the crystallized salt stock in salt pans
119 (samples 3 and 5) or purchased from the producers (samples 1 and 4). A seawater
120 sample was also collected from the sea shore in front of a pristine salt marsh located in
121 Torre la Sal, neighbouring a natural protected area (Natural Park of Ribera de Cabanes,
122 Spain), sited close to the city of Castellon (Sampling point 2). Sampling point 1 is a

123 solar saltwork sited in the Alfaques bay, south of the Ebro River delta. This river
124 receives domestic and industrial wastewater from numerous minor settlements along its
125 way. Discharges into the Ebro River vary at different locations, showing an increase
126 downstream, probably due to inputs from the tributaries or natural recharge of the
127 stream, and finally it flows into the Mediterranean sea after crossing through the Ebro
128 Delta [12]. Sampling point 3 is a solar saltwork located in the vicinity of an important
129 fishing and middle trade harbour, surrounded by a highly urbanized area. Sampling
130 points 4 and 5 are solar saltworks sited in high valuable natural areas but neighbouring
131 important summer touristic areas. All samples were stored at -20°C until analysis.

132

133 2.2. Reagents.

134 HPLC-grade water was obtained from a MilliQ water purification system (Millipore
135 Ltd., Bedford, MA, USA). Acetone, Ethyl Acetate, Dichlorometane (DCM) and n-
136 Hexane (ultra trace quality) used in solid-phase extraction (SPE) experiments were
137 purchased from Scharlab (Barcelona, Spain). Bond Elut cartridges C18 (500 mg)
138 (Varian, Harbor City, CA, USA) were used for SPE. Triphenyl phosphate (TPhP) and 2-
139 Ethylhexyl diphenyl phosphate (EHDPP) reference standards were purchased from TCI
140 Europe (Zwijndrecht, Belgium). Tri-n-butyl phosphate (TBP) and Tris(1-chloro-2-
141 propyl) phosphate (TCPP) reference standards were purchased from Sigma-Aldrich
142 (Madrid, Spain).

143

144 2.3. GC-TOF MS instrumentation.

145 GC system (Agilent 6890N; Agilent Palo Alto, USA) equipped with an autosampler
146 (Agilent 7683) was coupled to a time-of-flight mass spectrometer (GCT, Waters

147 Corporation, Manchester, U.K.), operating in electron ionization (EI). GC separation
148 was performed using a fused silica HP-5MS capillary column with a length of 30 m, an
149 internal diameter of 0.25 mm and a film thickness of 0.25 μm (J&W Scientific, Folsom,
150 CA, USA). The injector temperature was set to 280°C. Splitless injections of 1 μL
151 samples were carried out. Helium (99.999%; Carbueros Metálicos, Valencia, Spain) was
152 used as carrier gas at a flow rate of 1 mL/min. The interface and source temperature
153 were set to 250°C and a solvent delay of 4 min was selected.

154 The oven program in GC-TOF MS analysis was programmed as follows: 90 °C
155 (1min); 5 °C/ min to 300 °C (2 min). The TOF MS operated at 1 spectrum/s, acquisition
156 rate over the mass range m/z 50-650, using a multichannel plate voltage of 2850 V.
157 TOF-MS resolution was approximately 7000 (FWHM). Heptacosane standard, used for
158 the daily mass calibration and as lock mass, was injected via syringe in the reference
159 reservoir at 30°C for this purpose; the m/z ion monitored was 218.9856. The application
160 manager ChromaLynx and TargetLynx was used to process the qualitative data obtained
161 from standards and from sample analysis. Library search was performed using the NIST
162 02 Mass Spectral Library (www.nist.gov).

163

164 2.4. Recommended analytical procedure.

165 The recommended procedure is based on a generic sampling extraction procedure
166 previously applied for the determination of around 50 compounds, including
167 organochlorine and organophosphorus insecticides, herbicides, polychlorinated
168 biphenyls, polycyclic aromatic hydrocarbons, brominated diphenyl ethers, octyl/nonyl
169 phenols and pentachlorobenzene with some modifications [8]. Briefly, 62.5 g of salt
170 were diluted with water to a final volume of 250 mL and filtered. The filtered solution

171 was passed through the C₁₈ SPE cartridge, previously conditioned by passing 6 mL
172 methanol, 6 mL ethyl acetate:DCM (50:50), 6 mL methanol and 6 mL water avoiding
173 dryness. After loading the sample (250 mL), the cartridges were washed with 3 mL
174 water and dried by passing air under vacuum for at least 15 min. The elution was
175 performed by passing 5 mL ethyl acetate:DCM (50:50). The extract collected was
176 evaporated under a gentle nitrogen stream at 40°C and redissolved in 0.25 mL of n-
177 hexane. The overall procedure also involved a method blank to test that no
178 contamination was introduced in the extracts along the analysis.

179

180 2.5. GC-TOF MS methodology for non-target screening.

181 GC-TOF MS non-target screening was carried out by using the ChromaLynx
182 Application Manager. This software was used to detect the presence of multiple
183 components and to show its deconvoluted MS spectra to be submitted to library search
184 routine (in our case NIST 02 library). Components are reduced to a list of possible
185 candidates by using the list factor from the mass library search (library match >700).
186 Then, accurate mass confirmation is automatically performed. The formula from the
187 library list is submitted to an elemental composition calculator and accurate mass
188 measurements of (up to) 5 abundant ions are evaluated for confirmation/rejection of the
189 finding (for more details see [9, 10]).

190

191 **3. Results and Discussion**

192 3.1. Method performance

193 The analytical methodology described was applied to the analysis of one sea water and
194 four marine salt samples collected from different solar saltworks located along the

195 Spanish Mediterranean coast. The sensitive and reliable qualitative analysis was
196 favoured because of the 250-fold pre-concentration in the sample, with low sample
197 handling as corresponds to the SPE procedures, which was combined with the
198 advantages offered by GC-TOF MS. As shown in this paper and confirmed in our
199 previous works [10, 13], the non-target methodology applied for screening organic
200 contaminants is able to detect and identify a large number of GC-amenable compounds
201 belonging to different chemical families. However, a genuine non-target analysis is a
202 laborious and time-consuming task, as a consequence of the huge amount of
203 chromatographic peaks from the sample components and to the lack of list of
204 compounds to be searched. Therefore, the use of advanced processing software is
205 required to facilitate this task. This software should be able to detect relevant/abundant
206 sample components and to confirm their identity making use of the accurate full-
207 spectrum data provided by TOF MS. Although a part of the process can be performed
208 (almost) in an automated way, the expertise of the analyst on MS spectra interpretation
209 and the knowledge of the MS fragmentation rules are needed for a successful analysis
210 [9].

211

212 3.2. Positive findings in real samples

213 The samples analyzed contained volatile and semi volatile compounds, including
214 industrial sub-products, pesticides, flame retardants, plasticizers and personal care
215 products (**Table 1**). This kind of contaminants have been also found in other studies
216 related to water pollution, and they are into the environment as a consequence of
217 anthropogenic activities [4, 6, 10, 14-16].

218 **Table 1** shows the contamination pattern observed in the marine salt and seawater
219 samples studied in this work. The seawater sample collected from the sea shore at Torre
220 la Sal (S2), considered as a protected natural area relatively free of contaminant sources,
221 was almost free of the contaminants found in marine salt, and only two alkyl phenols
222 and one organic acid were identified. On the contrary, the marine salt samples were
223 more contaminated. The type of compounds detected seemed to vary according to the
224 geographical location of the saltwork.

225 As an illustrative example, **Table 2** shows the confirmation of identity of the
226 compounds detected in “Santa Pola” salt sample (S3). The elemental composition could
227 be proposed for at least four m/z fragment ions based on accurate mass measurements.
228 In addition, the experimental accurate mass for the main ions was compared with the
229 theoretical ones. In general, mass errors were below 3 mDa, except for a few low-
230 abundant ions. An example of the non-target detection of TCPP in “San Pedro del
231 Pinatar” salt sample is given in **Figure 2**. Five ions were selected from the EI spectrum
232 for the accurate mass confirmation of the identity of TCPP, with mass errors always
233 below 2.6 mDa. In addition, the chemical structure suggested for these ions was in
234 agreement with that of TCPP.

235 It is worth to notice that several of the compounds detected belong to the OPEs
236 family. These chemicals are produced in large quantities for their use as flame
237 retardants, plasticizers and also as pesticides. Their widespread use and presence in host
238 materials led to a continuous discharge and distribution through wastewaters [15], and
239 coastal areas are the fate of wastewaters from industrial and urban activities containing
240 these and other pollutants. As a consequence of the toxicity and environmental
241 persistence of OPEs, their presence in marine salt intended for human consumption
242 should be under control.

243 Considering the interest of OPEs, reference standards of TCPP, TBP, TPhP and
244 EHDPP were acquired in a subsequent step to perform additional experiments for
245 confirmation. We could not find the reference standard of bis(1-chloro-2-propyl) (3-
246 chloro-1-propyl)phosphate, which was also detected in the non-target screening. Using
247 reference standards it was feasible to test the retention time and to obtain their TOF MS
248 spectrum to unequivocally confirm the presence of these compounds in the samples.
249 The experiments with reference standards allowed us to confirm all positives previously
250 reported by TOF MS, demonstrating the excellent potential of this technique for
251 identificative purposes, even without reference standards.

252 As an illustrative example, **Figure 3** shows the eXtracted Ion Chromatograms
253 (XICs) for the positive of EHDPP detected in “La Trinitat Saltwork” salt sample (S1)
254 which could be additionally confirmed using the reference standard. The presence of the
255 chromatographic peaks in the XICs, at the expected retention time, and the attainment
256 of all Q/q ratios when comparing with the reference standard allowed the confirmation
257 of the finding in the sample. The corresponding EI accurate mass spectra generated by
258 TOF MS are also shown. Mass errors for four representative ions were below 3.2 mDa,
259 which gave more confidence to the confirmation process. Chemical structures for the
260 most abundant fragment ions were suggested based on the elemental compositions
261 proposed accordingly to the accurate mass measurements given by the instrument.

262 Apart from OPEs, the most abundant compounds detected were alkyl phenols.
263 Fragrances and plasticizers were also identified in some salt samples. The presence of
264 alkylphenols in aquatic environments has been previously reported by several authors
265 [9, 17, 18]. They are degradation products from alkylphenol polyethoxylates, mainly
266 applied to pesticide formulations and as plastic additives, among other uses [4]. The
267 persistence and accumulation properties of alkylphenols have led to their wide

268 distribution in different environmental compartments [19, 20]. The sources of these
269 pollutants are commonly the wastewaters from industrial and municipal treatment plants
270 [21] and their accumulation has been observed in sediments receiving contaminated
271 water flows [22]. The presence of these pollutants might pose a threat to the quality of
272 the salt produced in saltworks sited in environments like deltaic and estuarine locations
273 receiving water flows from industrial and/or urbanized areas. In fact, most detections of
274 alkylphenols corresponded to sampling points 1 and 3 (which accomplish these
275 characteristics; see description in Experimental section). Recently, Navarro et al. [6],
276 making use of GC-MS with single quadrupole, have detected several of these
277 compounds in the Ebro River sediments, in which delta the sampling point 1 is sited, as
278 indicated above.

279 The presence of Di-(2ethylhexyl)adipate in marine salts is also of concern. This
280 compound is used as plasticizer for food packaging, presents high toxicity for aquatic
281 organisms and is considered as endocrine disruptor [23], and it has been reported to be a
282 liver carcinogen in mice [24]. Another plasticizer detected, and also considered as
283 endocrine disruptor, was benzyl butyl phthalate. This compound has been previously
284 reported to be present in marine sediments [25]. Butylated hydroxytoluene (BHT) was
285 detected also in samples 3 and 4. This compound is an antioxidant widely used as food
286 additive and in biological samples for storage before analysis, as well as in cosmetics,
287 pharmaceuticals, jet fuels, among other uses [4], and it has been found in aquatic
288 environments [10, 26, 27].

289 2-Oxohexamethylenimine (caprolactam) -the monomer of nylon-6- has been
290 identified in marine salt samples probably due to the use of ammonium sulphate (a sub
291 product obtained during the manufacture of the polymer) in growing crops as fertilizer.
292 Methyl dihydrojasmonate and galaxolide were other compounds detected. They are

293 used as fragrances, and are included in the group of water contaminants called
294 Pharmaceuticals and Personal Care products (PPCPs), which are suspected to be an
295 environmental problem still not well known [28]. Similarly to other organic
296 contaminants, these compounds could be removed entirely or partly by means of
297 adequate technologies of wastewater treatment [16]. Dihydroactinidiolide, detected in
298 sample 4, is a volatile terpene occurring naturally in a variety of plants and insects, but
299 it has also been prepared synthetically for its use as a fragrance [29].

300 Other relevant compounds detected in marine salt were benzophenone and 3-
301 methyl-benzophenone, used as photoinitiator in UV-curing applications and as UV filter
302 [4]; cyclic octaatomic sulfur, indicator of microbiological activity [4]; and nonanoic
303 acid, used in the preparation of plasticizers and lacquers, and also as herbicide.

304 All identifications reported in this work were supported by accurate mass
305 measurements of several EI ions (up to five in most of the cases), by the low mass
306 errors observed in relation to their theoretical exact masses, and by the compatibility of
307 the chemical structures proposed for these ions with the chemical structure of the
308 compound identified.

309 The contamination pattern observed in the marine salt samples includes up to 25
310 organic compounds, with around 12 of them being present in every sample. Sources of
311 these contaminants surely are run offs from industries, farms and urbanized areas. Our
312 findings suggest an important presence of these pollutants into the environments around
313 the salt pans, which is in agreements with data reported in similar areas [28, 30, 31]. The
314 presence of the compounds identified in the marine salt samples indicates that they are
315 concentrated and that they persist along the crystallization process.

316

317 **4. Conclusion**

318 Without using any previous list of compounds to be investigated, the non-target
319 methodology applied in this work has allowed the detection and reliable identification
320 of several relevant contaminants of anthropogenic origin, belonging to quite different
321 chemical groups. The strong potential of GC-TOF MS for qualitative purposes comes
322 from the full spectrum acquisition at accurate mass, with satisfactory sensitivity,
323 provided by this instrument. Making an appropriate use of all relevant information
324 given by this technique it has been feasible to identify many contaminants in a reliable
325 way, even without reference standards being available, as illustrated in this work.
326 Surely, several of the compounds detected in marine salt would not had been detected
327 using a target approach, as although relevant they might not have been included in a
328 target screening, which is typically focused on a limited list of priority pollutants.

329 In the light of the results reported, we can conclude that priority pollutants,
330 typically subjected to strict control, constitute only part of the large chemical pollution
331 puzzle. There is a diverse group of unregulated pollutants, including industrial sub-
332 products, PPCPs, and an increasing concern on the risks that they pose on humans and
333 on the environment.

334

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341 MS instrument.

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343 **References**

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405 **Figure captions**

406

407 **Figure 1.** Area of study and sampling points

408

409 **Figure 2.** Detection of TCPP in the salt sample S5 by GC-TOF MS non-target
410 screening. (A) Extracted ion Chromatograms for five fragment ions. (B) Library mass
411 spectrum of TCPP at nominal mass. (C) Experimental EI accurate mass spectrum of the
412 positive finding of TCPP. Chemical structures proposed for the five most abundant EI
413 fragment ions and mass errors.

414

415 **Figure 3.** GC-TOF MS extracted ion chromatograms (top) at different m/z (mass
416 window 0.02 Da) and accurate mass spectrum (bottom) for EHDPP for the reference
417 standard (left) and for one positive salt sample (right). Q, qualitative ion; q,
418 confirmative ion; St, reference standard; S, sample; Q/q ratio within tolerance limits.
419 Chemical structures proposed for the most abundant fragment ions.

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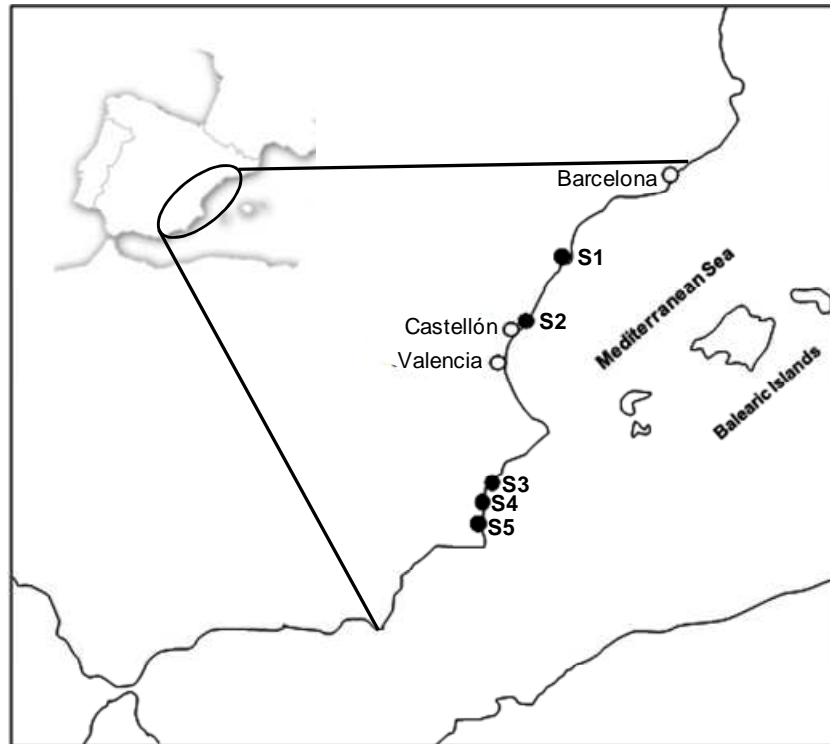
Table 1. Compounds identified in marine salt and seawater sample

Compound	CAS Number	S1	S2(w)	S3	S4	S5	Observations ^a
1-[4-(1-methylethenyl)phenyl]-Ethanone	5359-04-6	X			X	X	Industrial sub-product
2,4-di-tert-butylphenol	96-76-4		X	X			Toxic and dangerous for the environment, highly flammable, harmful and irritant.
2-[(Z)-3-hydroxy-3-methyl-1-butenyl]phenol	17235-14-2		X				Industrial sub-product
2-phenoxyethanol	122-99-6				X		Anesthetic
2-oxohexamethylenimine (Caprolactam)	105-60-2	X		X	X	X	Toxic by ingestion, inhalation, or absorption through the skin.
3,5-di-tert-butylphenol	1138-52-9				X		Antioxidants and light-protection agents
3,6-di-tert-butyl-4-ethylphenol	4130-42-1	X		X		X	Non toxic
3-methyl-benzophenone	134-84-9				X	X	UV filter. UV-curing applications
4,5,7-trichloro-2-methyl- benzofuran	18628-11-0				X	X	Pesticide
4-tert-amylphenol	80-46-6			X			Intermediate for organic mercury germicides pesticides and chemicals used in rubber and petroleum industries
4 -tert-octylphenol	140-66-9	X		X			Acutely very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment
Benzophenone	119-61-9	X			X		UV filter. UV-curing applications
Benzyl butyl phthalate	85-68-7					X	Plasticizer. Toxic effects such as cellular necrosis
Bis (1-chloro-2-propyl) (3-chloro-1-propyl) phosphate	137909-40-1	X		X			Pesticide, toxic and irritating
BHT	128-37-0			X	X		Synthetic antioxidant
Cyclic octaatomic sulfur	10544-50-0				X		Microbiological activity indicator ^a
Di (2-ethylhexyl) adipate	103-23-1					X	High toxicity to aquatic organisms
Dihydroactinidiolide	17092-92-1				X		Volatile terpene (large structure hydrocarbon)
EHDPP	1241-94-7	X		X			Pesticide, toxic to aquatic organisms
Galaxolide	1222-05-5	X			X		Musk fragrance
Methyl dihydrojasmonate	24851-98-7	X	X	X			Musk fragrance
Nonanoic acid	112-05-0			X			Irritant
TBP	126-73-8	X		X	X	X	Used as a herbicide and fungicide
TCPP	13674-84-5	X		X	X	X	Pesticide, flame retardant
TPhP	115-86-6	X		X			Pesticide, plasticizer and flame retardant

S1: Delta del Ebro (La Trinitat Saltworks), Tarragona; S2(w): Sea water from Torre la Sal Sea shore, Castellón; S3: Santa Pola Saltworks, Alicante; S4: Torrevieja Saltworks, Alicante; S5: San Pedro del Pinatar Saltworks, Murcia; ^a International Chemical Safety Cards: www.inchem.org/documents

Table 2. Confirmation of organic compounds in S3 salt sample.

Compound	N° CAS	Molecular peak		Ion 1		Ion 2		Ion 3		Ion 4		Ion 5	
		Molecular formula	Molecular mass	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)	Elemental composition	Experimental m/z (error in mDa)
2,4-di-tert-butylphenol	96-76-4	C ₁₄ H ₂₂ O	206.1671	C ₁₄ H ₂₂ O	206.1660 (-1.1)	C ₁₃ H ₂₀ O	192.1483 (-3.1)	C ₁₃ H ₁₉ O	191.1443 (0.7)	C ₁₁ H ₁₅ O	163.1120 (-0.3)	C ₉ H ₁₁ O	135.0802 (-0.8)
3,6-di-tert-butyl-4-ethylphenol	4130-42-1	C ₁₆ H ₂₆ O	234.1984	C ₁₆ H ₂₆ O	234.2013 (2.9)	C ₁₅ H ₂₄ O	220.1836 (0.9)	C ₁₅ H ₂₃ O	219.1760 (1.1)	C ₆ H ₆	78.0442 (-2.8)		
4-tert-octylphenol	140-66-9	C ₁₄ H ₂₂ O	206.1671	C ₉ H ₁₂ O	136.0857 (-3.1)	C ₉ H ₁₁ O	135.0798 (-1.2)	C ₈ H ₇ O	119.0475 (-2.2)	C ₇ H ₇ O	107.0496 (-0.1)		
4-tert-amylphenol	80-46-6	C ₁₁ H ₁₆ O	164.1201	C ₁₀ H ₁₃ O	149.0969 (0.3)	C ₉ H ₁₁ O	135.0810 (0)	C ₈ H ₉ O	121.0666 (1.3)	C ₇ H ₇ O	107.0486 (-1.1)	C ₆ H ₇ O	95.0477 (-2.0)
TCPP	13674-84-5	C ₉ H ₁₈ Cl ₅ O ₄ P	326.0008	C ₅ H ₁₁ O ₄ PCl	201.0100 (1.6)	C ₃ H ₇ O ₃ PCl	156.9818 (-0.3)	C ₂ H ₆ O ₄ P	125.0001 (-0.3)	H ₄ O ₄ P	98.9826 (-2.1)	C ₂ H ₅ OP	76.0058 (-3.0)
TPhP	115-86-6	C ₁₈ H ₁₅ O ₄ P	326.0708	C ₁₈ H ₁₅ O ₄ P	326.0737 (2.9)	C ₁₈ H ₁₄ O ₄ P	325.0656 (2.6)	C ₆ H ₆ O	94.0458 (3.9)	C ₆ H ₅	77.0375 (-1.6)		
TBP	126-73-8	C ₁₂ H ₂₇ O ₄ P	266.1647	C ₄ H ₁₂ O ₄ P	155.0480 (0.7)	C ₂ H ₆ O ₄ P	125.0019 (1.5)	H ₄ O ₄ P	98.9830 (-1.7)	C ₄ H ₈	56.0567 (-5.9)	C ₈ H ₂₀ O ₄ P	211.1109 (1.0)
Bis (1-chloro-2-propyl) (3-chloro-1-propyl) phosphate	137909-40-1	C ₉ H ₁₈ Cl ₅ O ₄ P	326.0008	C ₅ H ₉ ClO ₃ P	156.9818 (-0.3)	C ₂ H ₆ O ₄ P	125.0003 (-0.1)	C ₂ H ₅ Cl ₂ O ₃ P	116.9509 (0.1)	H ₄ O ₄ P	98.9828 (-1.9)	C ₂ H ₅ OP	76.0048 (3.0)
EHDPP	1241-94-7	C ₂₀ H ₂₇ O ₄ P	362.1647	C ₁₂ H ₁₂ O ₄ P	251.0457 (-1.6)	C ₁₂ H ₁₀ O	170.0750 (1.8)	C ₈ H ₁₆	112.1253 (0.1)	C ₆ H ₆ O	94.0412 (-0.7)	C ₆ H ₅	77.0366 (-2.5)
BHT	128-37-0	C ₁₅ H ₂₄ O	220.1827	C ₁₅ H ₂₄ O	220.1861 (3.4)	C ₁₄ H ₂₁ O	205.1611 (1.9)	C ₁₁ H ₁₃ O	161.0978 (1.2)	C ₁₁ H ₁₃	145.0983 (-3.4)		
2-oxohexamethylenimine (Caprolactam)	105-60-2	C ₆ H ₁₁ NO	113.0841	C ₆ H ₁₁ NO	113.0822 (-1.9)	C ₄ H ₇ NO	85.0555 (2.7)	C ₅ H ₈ O	84.0547 (-2.8)	C ₂ H ₂ NO	56.0169 (3.3)	C ₂ HNO	55.0116 (5.8)
Methyl dihydrojasmonate	24851-98-7	C ₁₃ H ₂₂ O ₃	226.1569	C ₁₃ H ₂₂ O ₃	226.1601 (3.2)	C ₈ H ₁₂ O ₃	156.0773 (-1.3)	C ₁₀ H ₁₇ O	153.1274 (-0.5)	C ₅ H ₇ O	83.0504 (0.7)		
Nonanoic acid	112-05-0	C ₉ H ₁₈ O ₂	158.1307	C ₇ H ₁₃ O ₂	129.0920 (0.4)	C ₆ H ₁₁ O ₂	115.0756 (-0.3)	C ₃ H ₅ O ₂	73.0258 (-3.2)	C ₂ H ₄ O ₂	60.0182 (-2.9)		



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430 *S1: Delta del Ebro (La Trinitat Saltworks), Tarragona*

431 *S2: Sea water from Torre la Sal Sea shore, Castellón*

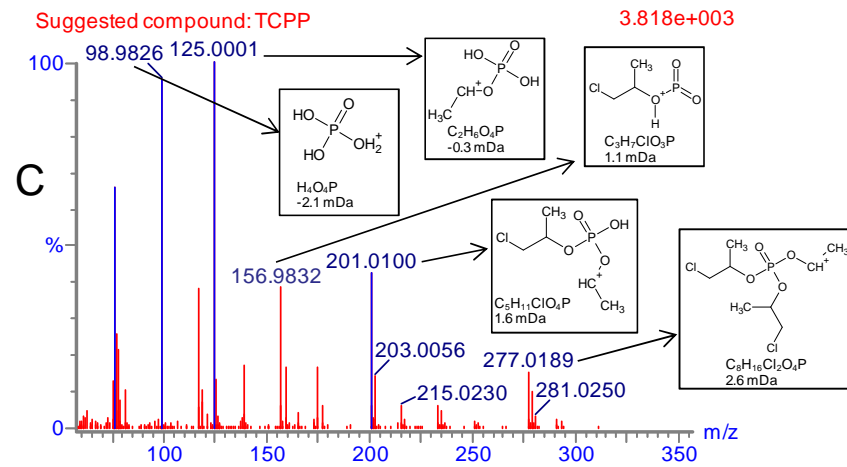
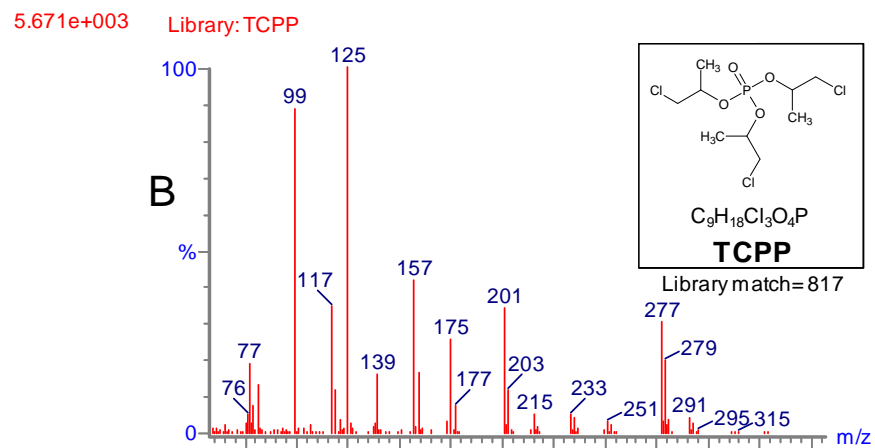
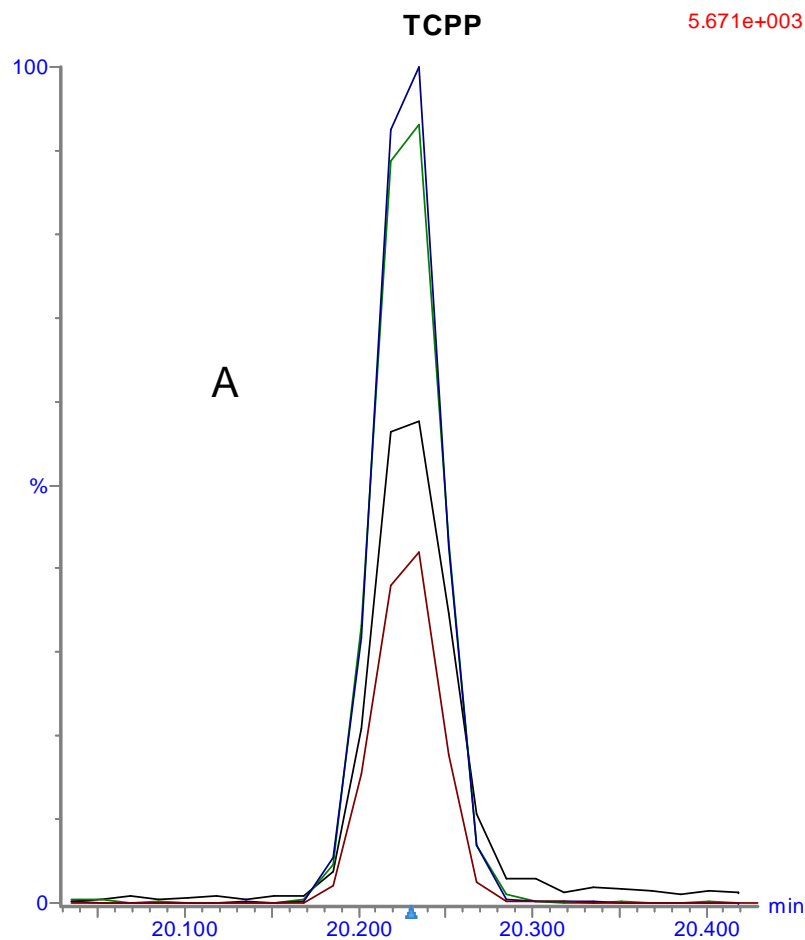
432 *S3: Santa Pola Saltworks, Alicante*

433 *S4: Torrevieja Saltworks, Alicante*

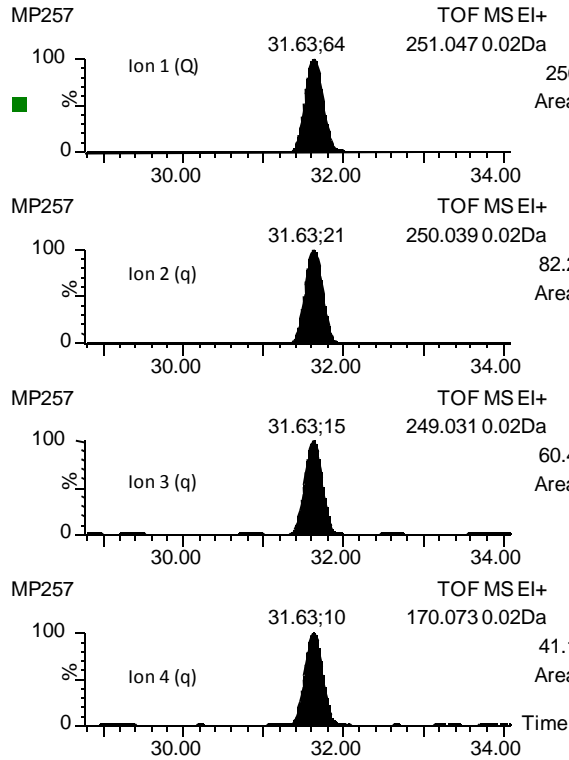
434 *S5: San Pedro del Pinatar Saltworks, Murcia*

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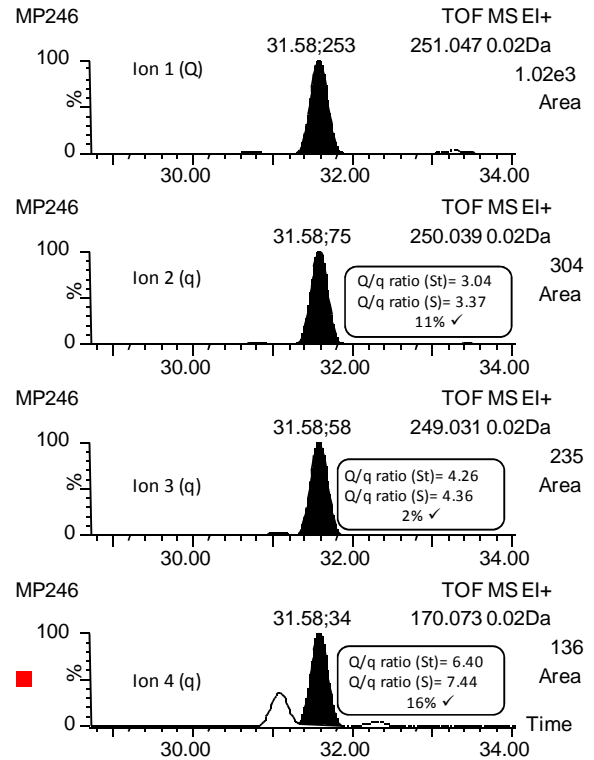
436 **Figure 1**



EHDPP Standard 1 mg/L

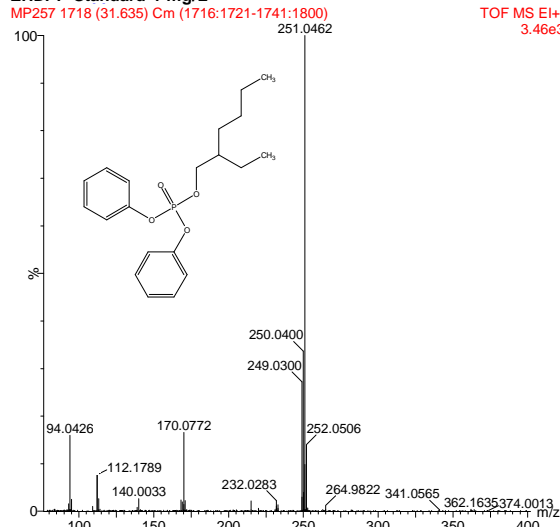


Salt sample from La Trinitat Saltworks

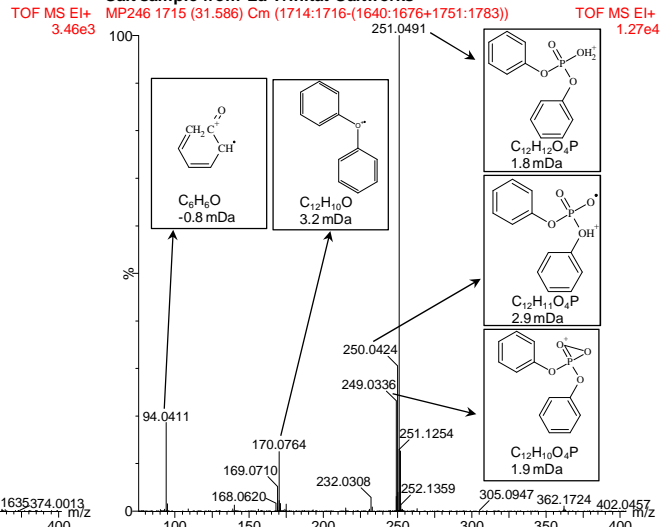


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EHDPP Standard 1 mg/L



Salt sample from La Trinitat Saltworks



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443 **Figure 3**

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