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# Simultaneous Testing of Multiclass Organic Contaminants in Food and Environment by Liquid Chromatography/ Dielectric Barrier Discharge Ionization- Mass Spectrometry

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# ABSTRACT

Dielectric Barrier Discharge Ionization (DBDI) LC/MS interface is based on the use of a low-temperature helium plasma, which features the possibility of simultaneous ionization of species with a wide variety of physicochemical properties. In this work, the performance of LC/DBDI-MS for trace analysis of highly relevant species in food and environment has been examined. Over 75 relevant species including multiclass priority organic contaminants and residues such as pesticides, polycyclic aromatic hydrocarbons, organochlorine species, pharmaceuticals, personal care products, and drugs of abuse were tested. LC/DBDI-MS performance for this application was assessed and compared with standard LC/MS sources (electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI)). The used benchtop Orbitrap mass spectrometer features a 10-Hz polarity switching mode, so that both positive and negative ion mode acquisitions are possible with acquisition cycles matching the requirements of fast liquid chromatography. Both polar and nonpolar species (including those typically analyzed by GC/electron ionization-MS) can be tested in a single run using polarity switching mode. The methodology was found to be effective to detect a wide array of organic compounds at concentration levels in the low ng $L^{-1}$ - µg $kg^{-1}$ range in wastewater and food matrices, respectively. Linearity was evaluated in olive oil extract, obtaining good correlation coefficients in the studied range. Additionally, minor matrix effects (≤ 15 % of signal suppression or enhancement) were observed for most of the studied analytes in this complex fatty matrix. The results obtained were compared with data from both ESI and APCI sources, obtaining a merged coverage between ESI and APCI in terms of analyte ionization and higher overall sensitivity for the proposed ion source based on DBD principle. The use of this approach further extends the coverage of current LC/MS methods towards an even larger variety of chemical species including both polar and nonpolar (non-ESI amenable) species and may find several applications in fields such as food, and environment testing or metabolomics where GC/MS and LC/MS are combined to cover as many different species as possible.



*Keywords*: dielectric barrier discharge, atmospheric pressure ionization, mass spectrometry, liquid chromatography, pesticide; environmental, food

# INTRODUCTION

Pesticide testing in food and environment samples requires the use of mass spectrometric techniques capable of ionizing a broad range of analytes. Until now, GC/MS and LC/MS coupled to electron ionization (EI) and electrospray ionization (ESI) sources were the most widely used techniques for the determination of organic residues and contaminants. The tendency towards more environmentally friendly and easy to degrade, i.e. more polar, chemicals has fostered impressive growth in the LC/MS market over the last 10 years. According to a study from Alder *et al.*[1], LC/MS offers better coverage than GC/MS for a vast selection of contaminants registered and monitored in Germany. In that study, it was shown that over 90% (453 of 500) of pesticides could be analyzed by LC/MS (ESI), whereas 73% (365 of 500) were amenable to GC/MS. There are, however, selected chemicals such as organochlorine or polycyclic aromatic hydrocarbons (PAHs) and other nonpolar non-ESI amenable chemicals that require the combined use of GC/MS and LC/MS. This is an issue for labs testing for pesticides in food and water, since both GC/MS and LC/MS instruments are necessary so that analyses have to be performed in duplicate. This scenario has led to the development of alternative ionization techniques for increased coverage of LC/MS towards less polar (GC amenable) compounds. LC/electron ionization (EI)-MS,[2-5] atmospheric pressure chemical ionization (APCI),[6] atmospheric pressure photoionization (APPI),[7-9] hybrid APCI/ESI and APPI/ESI sources,[10-14] atmospheric pressure laser ionization (APLI)[15,16] and its hybrid ESI/APLI interface,[17] and electrochemistry-assisted ESI[18-20] are amongst the technologies proposed as alternative and/or complementary sources to ESI.

Recently, an ion source for LC/MS based on dielectric barrier discharge principle [21,22] was reported by Hayen *et al.*[23] In this first report DBDI was used to ionize selected

species with different physicochemical properties such as PAHs, vitamins and amino acids in the positive ion mode. Interestingly, due to the different species generated in the plasma jet, the DBDI source offers the ability to generate not only positive but also negative ions, as various mechanisms including electron capture and proton transfer apply at the same time.[24-27] The eventual combination of this ionization source coupled to a mass spectrometer with a polarity switching ionization source (i.e. > 5-10 Hz) may provide a universal method covering a vast range of compounds with different physicochemical properties. In this article, we have evaluated the use of a dielectric barrier discharge plasma jet for this purpose. Two different scenarios demanding the combined use of GC/MS and LC/MS have been explored: pesticide testing in foodstuffs as well as priority contaminants in wastewater. The performance of DBDI source for multiclass multipolarity testing of organic contaminants and residues has been assessed using a high-resolution mass spectrometer (benchtop Orbitrap analyzer) with high-speed polarity switching.

## MATERIALS AND METHODS

**Standards and reagents.** Analytical grade standards of individual compounds were obtained from Sigma-Aldrich (Madrid, Spain). Individual pesticide or pharmaceutical stock solutions (*ca.* 300-400 mg $L^{-1}$) were prepared in methanol, acetonitrile or ethyl acetate and stored at -20 ºC. Commercially available standard solutions of drugs of abuse (Cerilliant, Round Rock, TX, USA) were diluted appropriately. Analytical standard containing a mixture of PAHs (PAH calibration mix, ref. 4-7940-U) in acetonitrile at 10 mg $L^{-1}$ was obtained from Supelco (Bellefonte, PA, USA). For LC/MS analysis, acetonitrile and methanol were obtained from Carl Roth (Karlsruhe, Germany). Formic acid (LC/MS quality) was obtained from Fluka (Buchs,

Switzerland). A Milli-Q-Plus ultra-pure water system from Millipore (Milford, MA, USA) was used throughout the study to obtain the HPLC-grade water used during the analyses. HPLC-grade acetonitrile for sample treatment and methanol for pesticide stock solutions were obtained from Merck (Darmstadt, Germany). Acetic acid was purchased from Panreac (Barcelona, Spain). Sodium chloride (reagent grade) was from J.T. Baker (Phillipsburg, NJ, USA). Anhydrous magnesium sulfate (reagent grade) was obtained from Fluka (Buchs, Switzerland). Primary-secondary amine (Supelclean™ PSA SPE bulk packing, 50 µm) was purchased from Supelco (Bellefonte, PA, USA). Florisil cartridges (1 g, 50 µm, 12 mL) and $C_{18}$ sorbent (50 µm) were obtained from Análisis Vínicos (Tomelloso, Ciudad Real, Spain). Oasis HLB™ SPE cartridges (200 mg, 6 mL) purchased from Waters (Milford, MA, USA) and a Supelco (Bellefonte, PA, USA) Visiprep™ SPE vacuum system were also used. A TurboVap LV concentration workstation (Caliper-Zymark, MA, USA) was used to evaporate the extracts.

**Sample preparation**

*Sample treatment for food commodities.* Variant procedures of the QuEChERS method (acronym of "quick, easy, cheap, effective, rugged and safe") were used to obtain orange or olive oil extracts. Buffered QuEChERS[28] procedure was used for oranges, while for olive oil it was used the QuEChERS procedure for fatty food matrices[29,30]. Detailed information of both employed procedures can be found in the Electronic Supplementary Material.

*Sample treatment for environmental samples.* The generic extraction method of wastewater matrices consisted of a solid-phase extraction with polymer based

hydrophilic-lipophilic balanced SPE cartridges (Oasis$^{TM}$ HLB). Detailed information of the employed procedure can be found in the Electronic Supplementary Material.

**Liquid chromatography/high resolution mass spectrometry.** The HPLC system consisted of an Accela$^{TM}$ HPLC including a vacuum degasser and a quaternary pump (Thermo Fisher Scientific, Bremen, Germany) connected to a CTC-CombiPAL$^{TM}$ autosampler (CTC Analytics GmbH, Zwingen, Switzerland). The separation of the species from the extracts was carried out at room temperature in a high pressure (600 bar) reversed-phase $C_{18}$ column (ZORBAX Eclipse XDB-C18 100 x 4.6 mm i.d., 1.8 μm, Agilent Technologies, Palo Alto, CA, USA) using a binary gradient. 20 μL of extract were injected in each study. Mobile phases A and B were water with 0.1% formic acid and acetonitrile with 0.1% formic acid, respectively. In the case of the olive oil determination, the chromatographic method held the initial mobile phase composition (30% B) constant for 2 min., followed by a linear gradient up to 85% B at 8 min. After that, it has been increased to 100% B at 20 min and was held at 100% B during 2 min. The flow rate was 500 μL min$^{-1}$. The chromatographic method for priority and emerging contaminants was slightly different. The initial mobile phase composition (10% B) was held constant for 2 min, followed by a fast gradient to reach 85% B at 8 min. After that, it increased to 100% B at 20 min and held at 100% B during 2 min.

**Dielectric barrier discharge ionization (DBDI) - mass spectrometry.** Mass spectrometric detection was carried out using a standalone benchtop Fourier transform orbitrap mass spectrometer (Exactive$^{TM}$) equipped with an Ion Max$^{TM}$ API source housing (Thermo Fisher Scientific, Bremen, Germany). The DBD microplasma ionization was carried out by modification of this API source. Microplasmas are

plasmas of small dimensions, *i.e*. at least one dimension is less than 1 mm. The diameter of the plasmajet used in this study is about 600 µm, and therefore it can be regarded as microplasma type. The implementation and operating conditions described elsewhere[23] are detailed as supporting information (Electronic Supplementary Material). The difference to the DBDI source used by Na *et al.*[31] for ambient mass spectrometry is that here two dielectric layers are in between the electrodes and the electrodes are wrapped around the capillary[24]. In the work of Na *et al.* a hollow stainless steel needle was used as electrode and to transport the gas, whereas the glass slide which is used as sample holder has the function of the dielectric barrier.

In contrast to the original set-up used by Hayen *et al.*[23], the teflon tube containing the DBD plasmajet was located in the left side of the source housing, in radial and not as previously in axial position regarding to the MS inlet capillary (**Figure 1**). This ion source, like the unmodified APCI source, works with a heated nebulizer maintained at 450 ºC. Nitrogen (99.999% purity) was used to nebulize the liquid eluent (sheath gas, flow rate set at 40.0 arbitrary units) and also to transport the finely dispersed sample droplets through the heated ceramic tube in which they were vaporized (auxiliary gas, flow rate set at 5.0 arbitrary units). Additionally, another nitrogen flow (sweep gas, flow rate of 2.0 arbitrary units) through the opposite direction of ions was used. The mass spectrometer was operated in full scan mode, acquiring data in the range *m/z* 140-500 with a resolving power of *ca.* 25,000 at *m/z* 200 (full width at half maximum, FWHM) and a maximum injection time of 250 ms. The full-scan data was recorded and processed with Xcalibur™ Version 2.1 software (Thermo Fisher Scientific, Bremen, Germany).

**<Figure 1>**

## RESULTS AND DISCUSSION

**Ionization and mass spectral features of DBDI-MS.** A suite of *ca.* 75 representative and highly relevant compounds were selected to accomplish the evaluation of the proposed LC/MS interface for food and environmental applications. Polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides, polar pesticides, emerging contaminants and drugs of abuse were amongst the classes of compounds tested. The spectral features of LC/DBDI-MS analysis of these compounds are summarized in **Tables 1-2** (and **Table S2**, Electronic Supplementary Material).

In the case of relatively polar species, $[M+H]^+$ was found as the dominant ion. This observation confirms that proton transfer is the main ionization mechanism and was observed for most of the pesticides and pharmaceuticals in the positive ion mode. Therefore, DBDI-MS can be regarded as gentle APCI-like ionization source.[24] This suggests that nitrogen plays an important role in the soft ionization process. The DBD plasma jet produces primary $N_2^+$ ions due to helium metastables. These $N_2^+$ ions generate protonated water clusters, which in turn protonate analyte molecules if they have higher proton affinity than water. Spatially-resolved optical emission measurements have been carried out to investigate this mechanism.[24,32,33] This pattern is also consistent with studies on ionization sources based on similar plasmas.[27,34]

In contrast, most of the PAHs exhibited the radical molecular ion ($[M]^{\cdot+}$) as the base peak. Radical cation formation could be attributed to direct charge exchange with $N_2^+$ ions formed in the plasma or by photoionization. In the case of acenaphthylene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene, indeno[123-cd]pyrene, the protonated molecule was also found, although the intensity was lower than that of

211 $[M]^{\cdot+}$. In the case of the non-polar compounds with low proton affinity (such as
212 hexachlorobenzene, pentachlorobenzene or ensodulfan sulfate), a different ionization
213 pattern can be envisaged. While organochlorine insecticide endosulfan sulfate exhibited
214 $[M-H]^-$ as main peak, both hexachlorobenzene and pentachlorobenzene exchanged one
215 chlorine atom with an oxygen ($[M-Cl+O]^-$).
216
217 In positive ion mode proton transfer is the dominating ionization mechanism, whereas
218 in the negative ion mode several other mechanisms are occurring. Potential ionization
219 mechanisms may include electron capture (EC), dissociative EC, and proton
220 abstraction.[35,36] It should be highlighted that the relative signal intensity in the negative
221 ionization mode is lower than in the positive ion mode. This could be attributed
222 amongst other reasons to the fact that the standard mobile phase combination selected
223 (water with formic acid and acetonitrile) is more suitable for positive ion formation.
224
225 Interestingly, the relative position of DBDI probe with regards to MS inlet (orifice) and
226 HPLC outlet (APCI heater probe) seems to play an important role on the mass spectral
227 features. In the previous study, using an axial positioning of the plasma jet (relative to
228 the MS inlet), a wide array of oxidized species was observed in the mass spectra of
229 PAHs.[23] In this previous study, signal obtained by DBDI of PAHs was distributed
230 among several others mainly based on oxygen addition. Adduct formation with
231 acetonitrile was also observed with polar compounds such as amino acids. These
232 phenomena constitute a disadvantage in terms of sensitivity and spectra interpretation
233 for identification purposes. These ions were not detected with the orthogonal
234 positioning of the plasma jet. The current source geometry configuration (see **Figure**

235 **1a**) allowed to obtain simpler mass spectra in most cases. This fact provides a
236 significant sensitivity enhancement and straightforward mass spectra interpretation.
237
238 **Analytical performance of LC/DBDI-MS for the multiclass determination of**
239 **organic contaminants in food and environment.** Three examples were tested:
240 multiclass organic contaminants in olive oil, priority and emerging contaminants in
241 wastewater effluents and multiclass pesticides in orange. The latter application of
242 LC/DBDI-MS analysis of pesticide in oranges as a non-fatty vegetable matrix will be
243 described solely in the Electronic Supplementary Material. The results obtained are
244 analog to the two other applications, but give additional support of the versatility of
245 LC/DBDI-MS.
246
247 *Multiclass detection of organic contaminants in virgin olive oil.* There are some
248 pesticides which are not ionized efficiently by ESI-based methods. This is the case of
249 endosulfan sulfate, an insecticide ubiquitous in olive oil,[37] or hexachlorobenzene. Both
250 compounds are not amenable by liquid chromatography coupled to atmospheric
251 pressure ionization mass spectrometry (LC/API-MS). Only, the use of direct electron
252 ionization (EI) interface for LC-MS has been reported for the simultaneous detection of
253 GC and LC amenable compounds in the same run without changes in the instrument
254 performance[5].
255 A detailed study by Thurman *et al*. reported that 1 µg of endosulfan injected on column
256 (40 µg/mL, 25 µL injected) gave no signal on ESI (+), ESI (-), APCI (+) or APCI (-)
257 using a full-scan instrument.[38] Although successful analysis of endosulfan sulfate by
258 LC/APCI-MS have been reported[39,40], these methods cannot be used to detect

259 endosulfan sulfate at reasonably low concentration level without excessive sample
260 preconcentration[39,40].
261 The detection of PAHs in edible oils is also of great relevance, but they cannot be
262 analyzed by LC/ESI-MS, thus requiring either a specific APCI, APPI, direct-EI or APLI
263 method or GC/MS. On the other hand, diuron and dimethoate are two agrochemicals
264 used on olives -and frequently found in olive oil- that do not work well with GC/EI-MS.
265 Therefore, the simultaneous analysis of these species cannot be straightforward
266 accomplished by a unique technique. LC/DBDI-MS, however, was found very effective
267 for their simultaneous analysis.
268
269 **Figure 2** shows an example of an olive oil extract spiked with 100 ng $g^{-1}$ of the targeted
270 contaminants. The olive oil sample was extracted using QuEChERS method for fatty
271 matrices. The final injected extract/sample ratio is 1 g $mL^{-1}$ extract, the standard one in
272 this type of analyses. The analysis was performed in polarity switching mode (10 Hz)
273 using a resolving power of ca. 25,000 (0.4 sec. acquisition time for each ionization
274 mode), so that all the results obtained (both positive and neagative ionization mode)
275 were collected in a single run (acquisition time of *ca.* 0.9 sec for both ionization modes).
276 The extracted ion chromatograms shown were reconstructed with a 20-ppm mass
277 window width. At the 100 µg $kg^{-1}$ level, all the tested species were detected. More than
278 20 compounds with different physicochemical properties were analyzed in one run.
279 Note that all the EIC traces exhibited signal-to-noise ratios distinctly far from the limit
280 of quantitation. **Table 1** shows the retention time, elemental composition, and
281 experimental mass error obtained in the measurement. Note that mass errors obtained
282 were within 2 ppm (relative mass error) with external calibration in most cases
283 regardless the ionization mode. This relative low average mass error provides the

284 unambiguous identification of each targeted species. The limits of detection (LOD)
285 obtained were in the range from 0.3 to 30 μg $kg^{-1}$ depending on the analyte. With
286 regards to the values obtained for pesticides in olive oil, limits of detection were below
287 or equal to 10 μg $kg^{-1}$ for all studied pesticides. In the case of PAHs, LODs were below
288 or equal to 20 μg $kg^{-1}$ for almost all studied compounds. Only acenaphthylene,
289 acenaphthene and phenanthrene showed higher LODs (25-30 μg $kg^{-1}$). Further
290 improvement may be achieved by using a triple quadrupole analyzer in the multiple
291 reaction monitoring mode, with a typical sensitivity increase of around one order of
292 magnitude, depending on the instrument. The linearity of the method was studied by
293 preparing matrix-matched standards across the range 10 - 400 μg $kg^{-1}$. Using DBDI
294 source correlation coefficients higher than 0.997 were obtained for all target analytes.
295 The comparison of the calibration slopes obtained in solvent-based and in matrix-
296 matched standards revealed minor signal enhancement or suppression, lower than 20%
297 (slope ratios typically in the range 0.8 – 1.2) in most cases, which is generally not
298 considered significant. These results (see detailed data in **Table S1** in the Electronic
299 Supplementary Material) are remarkable in such a complex fatty matrix. This example
300 on multiclass multipolarity detection of organic contaminants in olive oil shows the
301 versatility and potential of the ionization source for a wide array of different compounds
302 in complex samples.
303
304 **<Figure 2 and Table 1>**
305
306 *Simultaneous multiclass detection of priority and emerging organic contaminants in*
307 *effluent wastewater.* The proposed approach for multiclass widescope screening was
308 also evaluated for a demanding application such as effluent wastewater. Matrix-matched

309 standards were prepared using a SPE procedure involving a 50:1 preconcentration step.
310 **Table 2** includes the data for the studied compounds. As before, the accurate mass
311 measurements error were kept below 2 ppm in most cases, despite being undertaken at a
312 low concentration level (10 µg $L^{-1}$ in the extract) in a complex matrix and with the
313 polarity switching mode. The sensitivity attained was satisfactory in most cases. As an
314 example, **Figure S1** (Electronic Supplementary Material) shows the EIC of selected
315 pesticides and other priority and emerging contaminants in a wastewater effluent
316 extract. Polarity switching mode (10 Hz) using a resolving power of *ca.* 25,000 (0.4 sec.
317 acquisition time) was used for simultaneous acquisition in positive and negative
318 ionization modes. The extracted ion chromatograms were reconstructed with a 20-ppm
319 mass window width. For instance, triazine herbicides, drugs of abuse such as cocaine
320 and $\Delta^9$-THC, or antibiotics such as sulfadimethoxine or sulfathiazole exhibited signal-
321 to-noise ratio and peak area of *ca.* 2-3 orders of concentration above the limit of
322 detection. Considering the preconcentration factor, this would yield LODs in the low ng
323 $L^{-1}$ range. In constrast, the analytical signals of the compounds detected in the negative
324 ionization mode were lower, particularly in the case of pentachlorobenzene, with a LOD
325 approaching the concentration value tested. Another interesting compound was estrone,
326 which was detected as $[M+H]^+$, with a remarkable intense signal. Estrone usually needs
327 to lose a water molecule to be detected by ESI ($[M-H_2O+H]^+$), and with relatively low
328 ionization efficiency. The latter observation is another example of the potential
329 usefulness of the presented approach. A wide variety of chemicals could be tested at
330 low concentration levels in a single run.

331 **<Table 2 and Table 3>**

332

**Comparative evaluation of DBDI, APCI and ESI ionization for LC/MS analysis of multiclass organic contaminants.** With the aim of establishing the global capabilities of DBDI, a comparison with the most commonly used ionization sources was accomplished. A set of multiclass analytes covering both polar and nonpolar compounds detected in positive and negative ionization mode were tested in an olive oil extract. Analyses were performed with polarity switching mode using the Orbitrap instrument in the case of DBDI and APCI source. Data from ESI were obtained under default multiresidue method conditions using a LC/TOF-MS instrument with similar performance[41] or taken from previous data available for selected compounds [42,43]. The results obtained in the study are summarized in **Table 3**, and reveal that the DBDI approach compare well against the standard LC/MS ionization methods. DBDI ionization coverage falls in-between APCI and ESI, offering a good performance for both polar and nonpolar analytes. As expected, ESI could hardly detect relatively nonpolar species such as PAHs or organochlorine compounds. Only 6 out of the 24 compounds tested were amenable to ESI, while all the compounds tested were detected by DBDI. For these ESI-amenable compounds, the analytical performance in terms of analytical response was similar for both ESI and DBDI sources with LODs in the low μg $L^{-1}$ range.

In the case of APCI, all the compounds tested were detected with the exception of β-endosulfan. Interestingly, the analytical signal of each analyte under the same experimental conditions varied dramatically comparing APCI and DBDI. Overall, the sensitivity attained with DBDI was higher. In the case of relatively polar species such as dimethoate or malathion, the signal was nearly two orders of magnitude more intense with DBDI. These compounds are somewhat a marker of the general performance that

DBDI offers for relatively polar species, which often display $[M+Na]^+$ adducts in ESI, such as most of organophosphorus insecticides. Better sensitivity was also obtained for triazines and diuron. Low-molecular-weight PAHs were ionized more efficiently with DBDI (e.g. acenaphthene or phenanthrene), whereas APCI is advantageous for larger PAHs (and thus more nonpolar). In summary, DBDI offers appropriate performance for a wide array of compounds, covering polar compounds with a competitive performance with ESI and nonpolar species with a similar performance of APCI sources.

## CONCLUSIONS

In this article, the use of dielectric barrier discharge LC/MS interface for simultaneous ionization of compounds with a wide variety of physicochemical properties was evaluated. The combination of this ionization source with a fast-polarity switching high resolution mass spectrometer enabled the simultaneous acquisition in both positive and negative ion mode of polar and nonpolar compounds in a single run with acquisition cycles matching the requirements of liquid chromatography. Different applications including testing of multiclass contaminants in foodstuffs and the determination of priority and emerging contaminants in wastewater, which conventionally require the combined use of GC/MS and LC/MS instrumentation, were tested successfully in complex matrices, demonstrating the expanded ionization coverage of DBDI source towards multiclass detection species with remarkably different physicochemical properties. This expanded ionization coverage that offers good results of linearity and matrix effects in such a complex sample as olive oil, anticipates the application of DBDI for different fields which requires up to now the combined use of LC/ESI-MS and GC/MS such as food testing or metabolomics. Further work may include the optimization of the source and its positioning towards an increase in sensitivity for both

positive and negative ionization mode detection and a deeper understanding of both in-source fragmentation and ionization mechanisms. Comparative studies on matrix effects amongst different ionization sources will be also carry out in the future.

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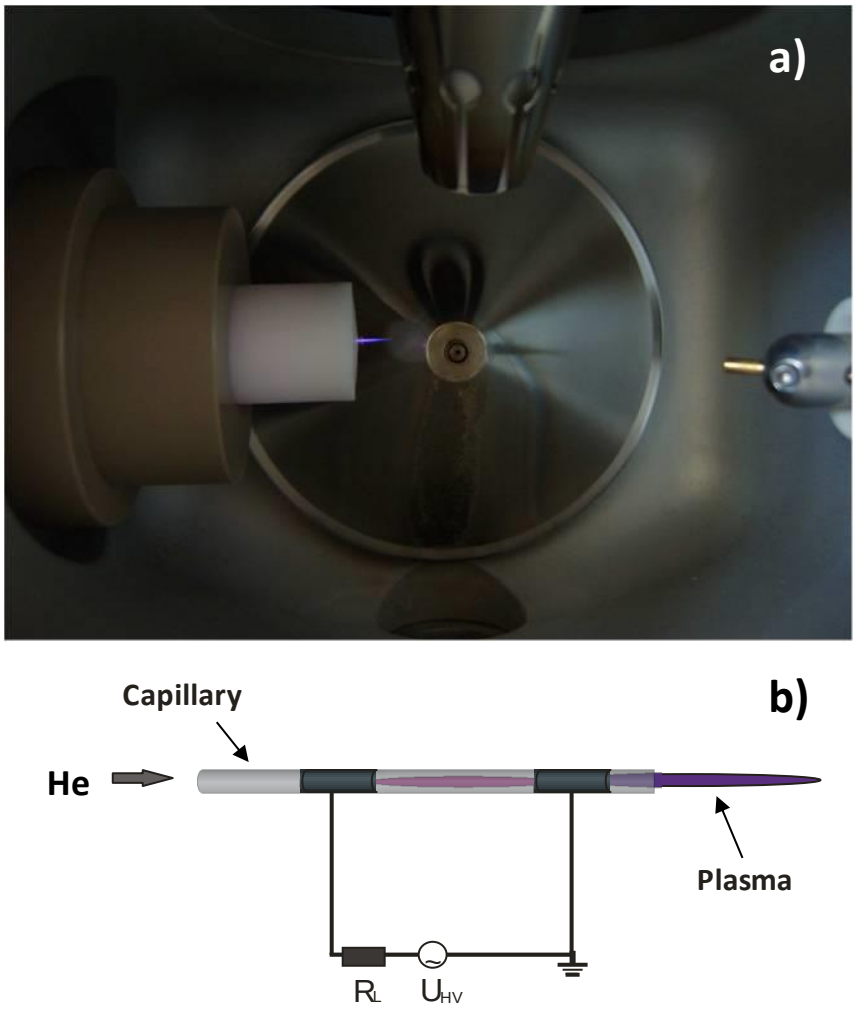
468

## Figure Captions

**Figure 1.** a) Positioning of the DBDI source (left) with respect to the MS inlet. b) Schematic outline of the DBDI probe.

**Figure 2.** LC/DBDI-MS analysis in polarity switching ionization mode of an olive oil extract spiked at 100 ng $g^{-1}$ (each) with a mixture of pesticides and PAHs. EICs corresponding to the following selected compounds: a) dimethoate, b) simazine, c) terbuthylazine, d) diuron, e) malathion, f) oxyfluorfen, g) endosulfan sulfate, h) hexachlorobenzene, i) fluoranthene and pyrene, j) fluorene, k) acenaphthylene, l) phenanthrene and anthracene, m) dibenzo[a,h]anthracene.

481 **Figure 1**

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485 **Figure 2**

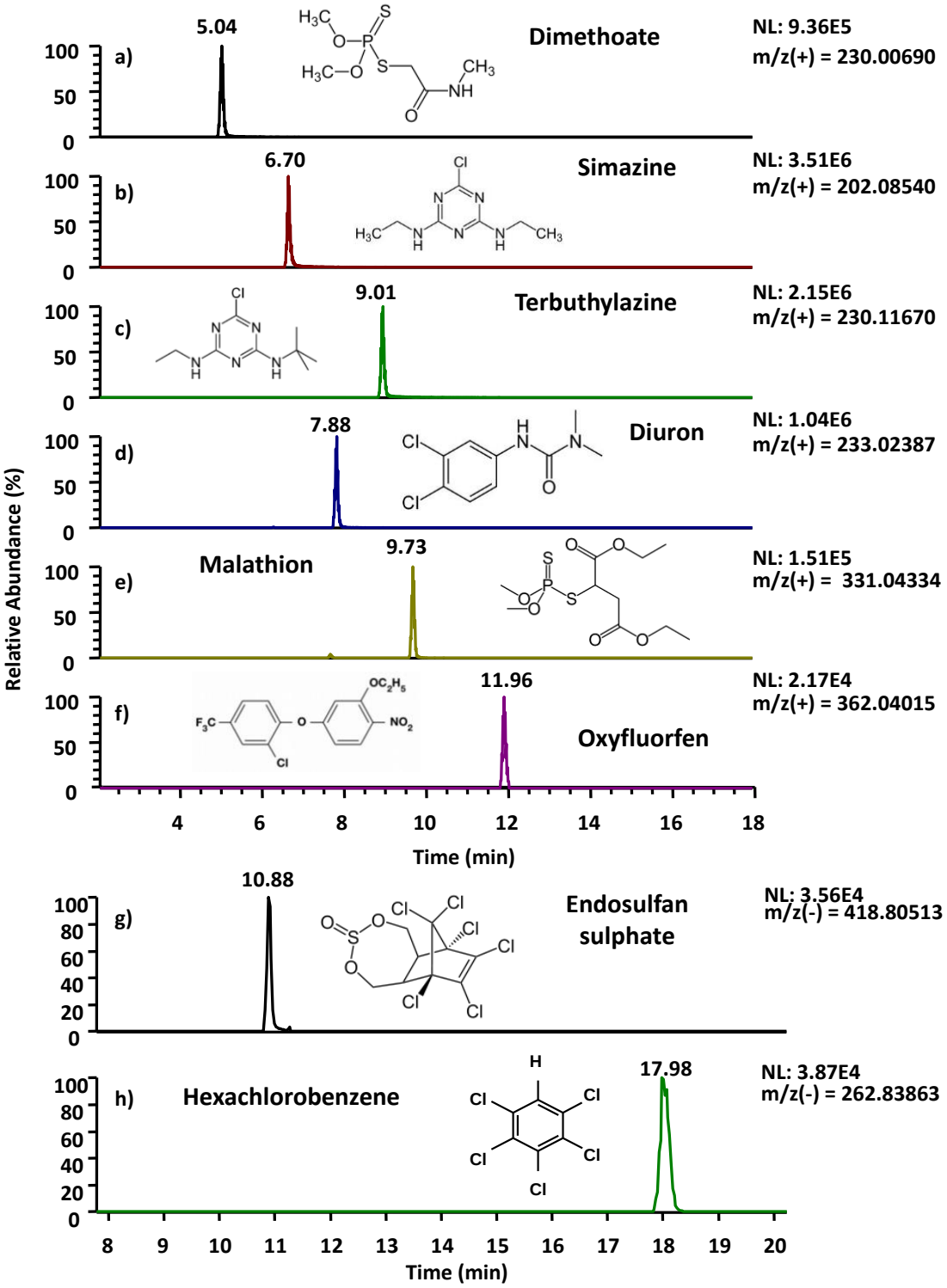


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**Figure 2 (cont)**

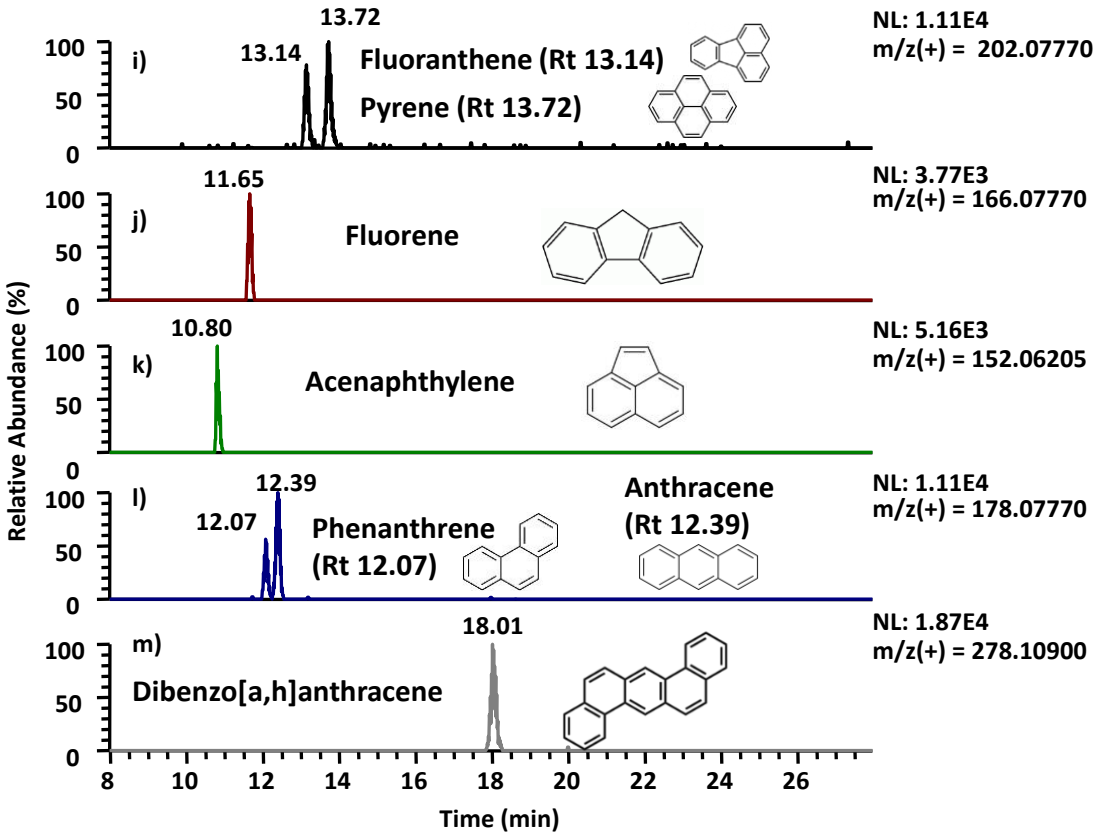


**Table 1.** LC/DBDI-MS analysis of multiclass pesticides and priority contaminants in an olive oil extract spiked at 100 µg $kg^{-1}$ (each). Simultaneous detection of positive and negative ions was accomplished using polarity switching acquisition mode.

| | Compound | Rt(min) | Ion | Formula ion | Theoretical *m/z* | Experim. *m/z* | Error ppm | LOD (µg $kg^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 1 | Dimethoate | 5.04 | $[M+H]^+$ | $C_5H_{13}NO_3PS_2$ | 230.00690 | 230.00660 | -1.3 | 0.3 |
| 2 | Simazine | 6.70 | $[M+H]^+$ | $C_7H_{13}N_5Cl$ | 202.08540 | 202.08527 | -0.6 | 0.5 |
| 3 | Diuron | 7.88 | $[M+H]^+$ | $C_9H_{11}Cl_2N_2O$ | 233.02429 | 233.02387 | -1.8 | 0.3 |
| 4 | Terbuthylazine | 8.99 | $[M+H]^+$ | $C_9H_{17}ClN_5$ | 230.11670 | 230.11656 | -0.7 | 0.5 |
| 5 | Malathion | 9.73 | $[M+H]^+$ | $C_{10}H_{20}O_6PS_2$ | 331.04334 | 331.04315 | -0.6 | 25 |
| 6 | Acenaphtylene | 10.80 | $[M]^{\bullet+}$ | $C_{12}H_8$ | 152.06205 | 152.06183 | -1.5 | 30 |
| 7 | Endosulfan sulfate | 10.91 | $[M-H]^-$ | $C_9H_5Cl_6SO_4$ | 418.80452 | 418.80513 | 1.5 | 6.5 |
| 8 | Fluorene | 11.65 | $[M]^{\bullet+}$ | $C_{13}H_{10}$ | 166.07770 | 166.07707 | -3.8 | 10 |
| 9 | Acenaphthene | 11.88 | $[M]^{\bullet+}$ | $C_{12}H_{10}$ | 154.07770 | 154.07738 | -2.1 | 25 |
| 10 | Oxyfluorfen | 11.97 | $[M+H]^+$ | $C_{15}H_{12}ClF_3NO_4$ | 362.04015 | 362.03964 | -1.4 | 1 |
| 11 | Phenanthrene | 12.08 | $[M]^{\bullet+}$ | $C_{14}H_{10}$ | 178.07770 | 178.07760 | -0.6 | 25 |
| 12 | Anthracene | 12.39 | $[M]^{\bullet+}$ | $C_{14}H_{10}$ | 178.07770 | 178.07756 | -0.8 | 20 |
| 13 | Fluoranthene | 13.13 | $[M]^{\bullet+}$ | $C_{16}H_{10}$ | 202.07770 | 202.07758 | -0.6 | 16 |
| 14 | Pyrene | 13.72 | $[M]^{\bullet+}$ | $C_{16}H_{10}$ | 202.07770 | 202.07759 | -0.6 | 12.5 |
| 15 | Benz[a]anthracene | 14.70 | $[M]^{\bullet+}$ | $C_{18}H_{12}$ | 228.09335 | 228.09277 | -2.6 | 6 (a) |
| 16 | Chrysene | | | | | | | |
| 17 | Benzo[b]fluoranthene | 16.49 | $[M]^{\bullet+}$ | $C_{20}H_{12}$ | 252.09335 | 252.09311 | -1.0 | 10 |
| 18 | Benzo[k]fluoranthene | 16.73 | $[M]^{\bullet+}$ | $C_{20}H_{12}$ | 252.09335 | 252.09303 | -1.3 | 10 |
| 19 | Benzo[a]pyrene | 17.40 | $[M+H]^+$ | $C_{20}H_{13}$ | 253.10118 | 253.10103 | -0.6 | |
| | | | $[M]^{\bullet+}$ | $C_{20}H_{12}$ | 252.09335 | 252.09290 | -1.8 | 10 |
| 20 | Hexachlorobenzene | 18.00 | $[M^{\cdot}Cl+O]^-$ | $C_6Cl_5O$ | 262.83863 | 262.83979 | 0.2 | 5 |
| 21 | Dibenzo[a,h]anthracene | 18.00 | $[M+H]^+$ | $C_{22}H_{15}$ | 279.11683 | 279.11567 | -4.1 | |
| | | | $[M]^{\bullet+}$ | $C_{22}H_{14}$ | 278.10900 | 278.10851 | -1.8 | 10 |
| 22 | Benzo[ghi]perylene | 19.52 | $[M+H]^+$ | $C_{22}H_{13}$ | 277.10118 | 277.10054 | -2.3 | |
| | | | $[M]^{\bullet+}$ | $C_{22}H_{12}$ | 276.09335 | 276.09292 | -1.6 | 10 |
| 23 | Indeno[1,2,3-cd] pyrene | 19.90 | $[M+H]^+$ | $C_{22}H_{13}$ | 277.10118 | 277.10134 | 0.6 | |
| | | | $[M]^{\bullet+}$ | $C_{22}H_{12}$ | 276.09335 | 276.09295 | -1.5 | 10 |

(a) Sum of benz[a]anthracene and chrysene. Both compounds coelute in the same chromatographic peak.

**Table 2.** LC/DBDI-MS analysis of multiclass priority and emerging contaminants in an effluent wastewater sample extract spiked at 10 µg $L^{-1}$ (each). Simultaneous detection of positive and negative ions was accomplished using polarity switching acquisition mode. n.d., not detected

| | Compound | Rt (min) | Ion | Formula ion | Theoretical *m/z* | Experim. *m/z* | Error ppm | Area |
|---|---|---|---|---|---|---|---|---|
| 1 | Sulfathiazole | 6.03 | $[M+H]^+$ | $C_9H_{10}N_3O_2S_2$ | 256.02089 | 256.02157 | 2.6 | 3.80E+05 |
| 2 | Antipyrine | 6.44 | $[M+H]^+$ | $C_{11}H_{13}N_2O$ | 189.10224 | 189.10238 | 0.7 | 1.63E+06 |
| 3 | Cocaine | 6.50 | $[M+H]^+$ | $C_{17}H_{22}NO_4$ | 304.15433 | 304.15485 | 1.7 | 1.02E+06 |
| 4 | Propanolol | 6.80 | $[M+H]^+$ | $C_{16}H_{22}NO_2$ | 260.16451 | 260.16491 | 1.6 | 8.41E+05 |
| 5 | Dimethoate | 7.21 | $[M+H]^+$ | $C_5H_{13}NO_3PS_2$ | 230.00690 | 230.00716 | 1.1 | 5.23E+04 |
| | | 7.22 | Frg. 1 | $C_4H_8O_3PS_2$ | 198.96470 | 198.96523 | 2.7 | 1.59E+05 |
| | | 7.22 | Frg. 2 | $C_3H_8O_2PS_2$ | 170.96978 | 170.97024 | 2.7 | 7.90E+04 |
| 6 | Sulfadimethoxin | 7.75 | $[M+H]^+$ | $C_{12}H_{15}N_4O_4S$ | 311.08085 | 311.08130 | 1.4 | 1.49E+06 |
| 7 | Metoxuron | 7.80 | $[M+H]^+$ | $C_{10}H_{14}ClN_2O_2$ | 229.07383 | 229.07407 | 1.0 | 6.57E+05 |
| 8 | Ametryn | 8.00 | $[M+H]^+$ | $C_9H_{18}N_5S$ | 228.12774 | 228.12772 | -0.1 | 1.34E+06 |
| | | 8.00 | Frg. 1 | $C_6H_{12}N_5S$ | 186.08079 | 186.08082 | 0.1 | 1.67E+05 |
| 9 | Monuron | 8.12 | $[M+H]^+$ | $C_9H_{12}ClN_2O$ | 199.06327 | 199.06341 | 0.7 | 3.55E+05 |
| 10 | Chlortoluron | 8.69 | $[M+H]^+$ | $C_{10}H_{14}ClN_2O$ | 213.07892 | 213.07938 | 2.2 | 6.10E+05 |
| 11 | Flumeturon | 8.70 | $[M+H]^+$ | $C_{10}H_{12}F_3N_2O$ | 233.08962 | 233.08972 | 0.4 | 7.02E+05 |
| 12 | Tamoxifen | 8.75 | $[M+H]^+$ | $C_{26}H_{30}NO$ | 372.23219 | 372.23300 | 2.2 | 7.26E+05 |
| 13 | Isoproturon | 8.87 | $[M+H]^+$ | $C_{12}H_{19}N_2O$ | 207.14919 | 207.14934 | 0.7 | 1.30E+06 |
| | | 8.86 | Frg. 1 | $C_9H_{13}N_2O$ | 165.10224 | 165.10225 | 0.1 | 1.98E+05 |
| 14 | Atrazine | 8.98 | $[M+H]^+$ | $C_8H_{15}ClN_5$ | 216.10105 | 216.10106 | <0.1 | 3.43E+06 |
| | | 8.99 | Frg. 1 | $C_5H_9ClN_5$ | 174.05410 | 174.05425 | 0.9 | 5.35E+05 |
| 15 | Ethoxyquin | 9.05 | $[M+H]^+$ | $C_{14}H_{20}NO$ | 218.15394 | 218.15404 | 0.5 | 7.13E+05 |
| 16 | Buturon | 9.37 | $[M+H]^+$ | $C_{12}H_{14}ClN_2O$ | 237.07892 | 237.07899 | 0.3 | 8.39E+05 |
| 17 | Estrone | 9.40 | $[M+H]^+$ | $C_{18}H_{23}O_2$ | 271.16926 | 271.16919 | -0.2 | 2.90E+05 |
| 18 | Propazine | 9.66 | $[M+H]^+$ | $C_9H_{17}ClN_5$ | 230.11670 | 230.11659 | -0.4 | 1.55E+06 |
| | | 9.65 | Frg. 1 | $C_6H_{11}ClN_5$ | 188.06975 | 188.07000 | 1.3 | 2.75E+05 |
| | | 9.65 | Frg. 2 | $C_3H_5ClN_5$ | 146.02280 | 146.02288 | 0.6 | 3.56E+04 |
| 19 | Terbuthylazine | 9.82 | $[M+H]^+$ | $C_9H_{17}ClN_5$ | 230.11670 | 230.11644 | -1.1 | 1.48E+06 |
| | | 9.82 | Frg. 1 | $C_5H_9ClN_5$ | 174.05410 | 174.05398 | -0.7 | 5.95E+05 |
| 20 | Linuron | 9.84 | $[M+H]^+$ | $C_9H_{11}Cl_2N_2O_2$ | 249.01921 | 249.01906 | -0.6 | 3.16E+05 |
| | | 9.85 | Frg. 1 | $C_8H_7N_2Cl_2$ | 200.99808 | 200.99765 | -2.1 | 4.14E+04 |
| 21 | Mecarbam | 10.00 | $[M+H]^+$ | $C_{10}H_{21}NO_5PS_2$ | 330.05933 | n.d. | -- | -- |
| | | 10.00 | Frg. 1 | $C_7H_{16}O_4PS_2$ | 259.02221 | 259.02211 | -0.4 | 2.23E+04 |
| 22 | Malathion | 10.30 | $[M+H]^+$ | $C_{10}H_{20}O_6PS_2$ | 331.04334 | 331.04246 | -2.7 | 1.93E+04 |
| | | 10.29 | Frg. 1 | $C_8H_{14}O_5PS_2$ | 285.00148 | 285.00135 | -0.4 | 3.79E+04 |
| | | 10.29 | Frg. 2 | $C_7H_{14}O_4PS_2$ | 257.00656 | 257.00663 | 0.3 | 2.49E+04 |
| 23 | Procymidone | 10.48 | $[M+H]^+$ | $C_{13}H_{12}Cl_2NO_2$ | 284.02396 | 284.02290 | -3.7 | 4.60E+03 |
| 24 | Alachlor | 10.72 | $[M+H]^+$ | $C_{14}H_{21}ClNO_2$ | 270.12553 | 270.12555 | 0.1 | 3.99E+04 |
| | | 10.72 | Frg. 1 | $C_{13}H_{17}ONCl$ | 238.09932 | 238.09923 | -0.4 | 5.12E+05 |
| | | 10.72 | Frg. 2 | $C_{11}H_{16}N$ | 162.12773 | 162.12759 | -0.8 | 3.28E+05 |
| 25 | Gemfibrizil | 11.12 | $[M-H]^-$ | $C_{15}H_{21}O_3$ | 249.14962 | 249.14985 | 0.9 | 6.03E+04 |
| 26 | Tributhyl phosphate | 11.35 | $[M+H]^+$ | $C_{12}H_{28}PO_4$ | 267.17197 | 267.17171 | -1.0 | 5.79E+05 |
| 27 | Diazinon | 11.67 | $[M+H]^+$ | $C_{12}H_{22}N_2O_3PS$ | 305.10833 | 305.10809 | -0.8 | 1.21E+06 |
| | | 11.66 | Frg. 1 | $C_{10}H_{18}O_3N_2PS$ | 277.07703 | 277.07685 | -0.6 | 1.69E+05 |
| | | 11.66 | Frg. 2 | $C_8H_{14}O_3N_2PS$ | 249.04573 | 249.04561 | -0.5 | 5.61E+04 |
| | | 11.66 | Frg. 3 | $C_8H_{13}N_2O$ | 153.10224 | 153.10207 | -1.1 | 2.36E+05 |
| 28 | Fenofibrate | 13.35 | $[M+H]^+$ | $C_{20}H_{22}ClO_4$ | 361.12011 | 361.11989 | -0.6 | 3.19E+05 |
| 29 | Delta-9-THC | 15.94 | $[M+H]^+$ | $C_{21}H_{31}O_2$ | 315.23186 | 315.23183 | -0.1 | 1.00E+06 |
| 30 | Pentachlorobenzene | 16.09 | $[M-Cl+O]^-$ | $C_6HCl_4O$ | 228.87870 | 228.87869 | <0.1 | 6.74E+03 |
| 31 | Hexachlorobenzene | 18.23 | $[M-Cl+O]^-$ | $C_6Cl_5O$ | 262.83973 | 262.84027 | 2.1 | 1.82E+04 |

**Table 3.** Comparative evaluation of DBDI ionization source with APCI and Electrospray interfaces for LC/MS analysis of multiclass organic contaminants. An olive oil extract (1 mL $g^{-1}$ matrix concentration) spiked at 100 µg $kg^{-1}$ was used for comparison with APCI source.

| Compound | | Rt | Polarity | DBDI vs APCI([a]) | DBDI vs ESI([b]) | |
|---|---|---|---|---|---|---|
| | | | | Peak area ratio DBDI/APCI | LOD DBDI (olive oil) µg $L^{-1}$ | LOD ESI ([b]) ([e]) (neat standards) µg $L^{-1}$ |
| 1 | Acenaphthene | 11.88 | + | 5.3 | 25 | -([e]) |
| 2 | Acenaphthylene | 10.80 | + | 1.2 | 30 | -([e]) |
| 3 | Fluorene | 9.65 | + | 1.8 | 10 | -([e]) |
| 4 | Anthracene | 12.40 | + | 1.0 | 20 | -([e]) |
| 5 | Phenanthrene | 12.08 | + | 6.4 | 25 | -([e]) |
| 6 | Benz[a]anthracene/ | | | | | |
| 7 | Chrysene | 14.70 | + | 0.7 | 6 ([d]) | -([e]) |
| 8 | Benzo[a]pyrene | 17.40 | + | 0.3 | 10 | -([e]) |
| 9 | Benzo[b]fluoranthene | 16.46 | + | 1.4 | 10 | -([e]) |
| 10 | Benzo[k]fluoranthene | 16.73 | + | 0.6 | 10 | -([e]) |
| 11 | Dibenzo[a,h]anthracene | 18.00 | + | 0.2 | 10 | -([e]) |
| 12 | Benzo[ghi]perylene | 19.52 | + | 0.2 | 10 | -([e]) |
| 13 | Indeno[1,2,3-cd]pyrene | 19.90 | + | 0.2 | 10 | -([e]) |
| 14 | Fluoranthene | 13.13 | + | 1.0 | 16 | -([e]) |
| 15 | Pyrene | 13.72 | + | 0.7 | 12.5 | -([e]) |
| 16 | Terbuthylazine | 9.00 | + | 3.2 | 0.5 | 0.3([b]) |
| 17 | Simazine | 6.70 | + | 4.4 | 0.5 | 0.3([b]) |
| 18 | Diuron | 7.90 | + | 3.1 | 0.3 | 0.3([b]) |
| 19 | Dimethoate | 5.10 | + | 113.1 | 0.3 | 0.3([b]) |
| 20 | Malathion | 9.73 | + | 66.6 | 2.5 | 0.3([b]) |
| 21 | Oxyfluorfen | 11.97 | + | 1.1 | 1 | 20 |
| 22 | Endosulfan sulfate | 10.91 | - | 0.7 | 6.5 | -([e]) |
| 23 | beta-Endosulfan | 9.47 | - | -- ([c]) | 25 | -([e]) |
| 24 | Hexachlorobenzene | 18.00 | - | 0.4 | 5 | -([e]) |

([a]) An olive oil extract (1 mL $g^{-1}$ matrix concentration) spiked at 100 µg $kg^{-1}$ was used for comparison of DBDI source with APCI source. Peak area ratio under the same conditions (using XIC with a narrow mass window of ± 5 mDa) was used for this comparison.

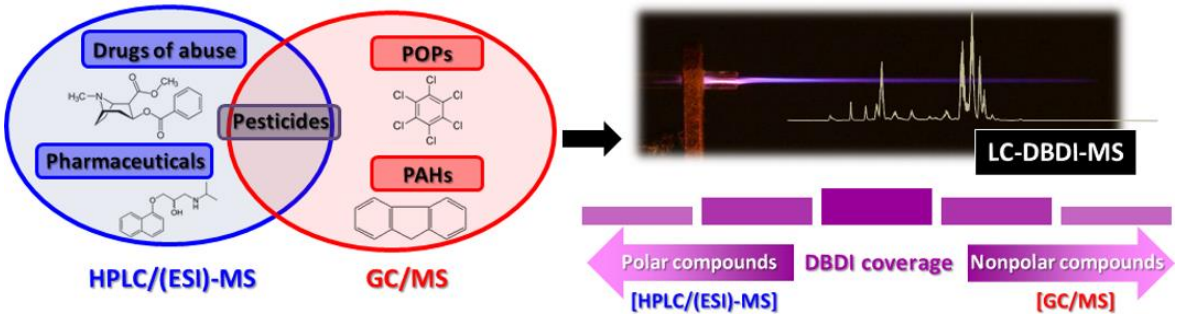
([b]) Comparative evaluation of DBDI and ESI presented is based on data reported (41,42) with the same instrument (when available) using neat standards.

([c]) Not detected in APCI analysis/only detected with DBDI at the concentration level tested.

([d]) Sum of benz[a]anthracene and chrysene. Both compounds coelute in the same chromatographic peak.

([e]) Experiments carried out using a LC-ESI-TOF-MS under general default multianalyte conditions (37) did not yielded any signal for the mentioned analytes, which are considered elsewhere as non-electrospray amenable.

**Graphical abstract for TOC Entry**




**Ultratrace detection of multiclass organic contaminants using LC/MS with dielectric barrier discharge ionization**