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PAPER

Simultaneous testing of multiclass organic contaminants in food and environment by liquid chromatography/dielectric barrier discharge ionization-mass spectrometry†

Bienvenida Gilbert-López,[a] Juan F. García-Reyes,[b] Cordula Meyer,[a] Antje Michels,[a] Joachim Franzke,[a] Antonio Molina-Díaz*[b] and Heiko Hayen*[c]

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A 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 in detecting a wide array of organic compounds at concentration levels in the low ng L^{-1} to μg kg^{-1} range in wastewater and food matrices, respectively. The linearity was evaluated in an 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 the 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.

Introduction

Pesticide testing in food and environmental 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 have been 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 and therefore analyses have to be performed in duplicate. This

[a]*Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Otto-Hahn-Str. 6b, 44227 Dortmund, Germany*
[b]*Analytical Chemistry Research Group (FQM-323), Department of Physical and Analytical Chemistry, University of Jaén, Campus Las Lagunillas, Edif. B-3, 23071 Jaén, Spain. E-mail: amolina@ujaen.es; Fax: +34 953 212940; Tel: +34 953 212147*
[c]*University of Wuppertal, Department of Food Chemistry, 42119 Wuppertal, Germany. E-mail: hayen@uni-wuppertal.de; Fax: +49 202 4393073; Tel: +49 202 4393457*
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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 the 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 requiring 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 the 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 °C. Commercially available standard solutions of drugs of abuse (Cerilliant, Round Rock, TX, USA) were diluted appropriately. An 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. The buffered QuEChERS[28] procedure was used for oranges, while for olive oil the QuEChERS procedure for fatty food matrices was used.[29,30] Detailed information on both employed procedures can be found in the ESI.†

Sample treatment for environmental samples. The generic extraction method of wastewater matrices consisted of solid-phase extraction with polymer based hydrophilic–lipophilic balanced SPE cartridges (Oasis™ HLB). Detailed information on the employed procedure can be found in the ESI.†

Liquid chromatography/high resolution mass spectrometry

The HPLC system consisted of an Accela™ HPLC including a vacuum degasser and a quaternary pump (Thermo Fisher Scientific, Bremen, Germany) connected to a CTC-CombiPAL™ 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 × 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. The mobile phases A and B were water with 0.1% formic acid and acetonitrile with 0.1% formic acid, respectively. In the case of 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 was increased to 100% B at 20 min and held at 100% B for 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 was increased to 100% B at 20 min and held at 100% B for 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™) equipped with an Ion Max™ 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 plasma jet used in this study was about 600 μm, and therefore it can be regarded as the microplasma type. The implementation and operating conditions described elsewhere[23] are detailed in the ESI.† The difference from the DBDI source used by Na *et al.*[31]

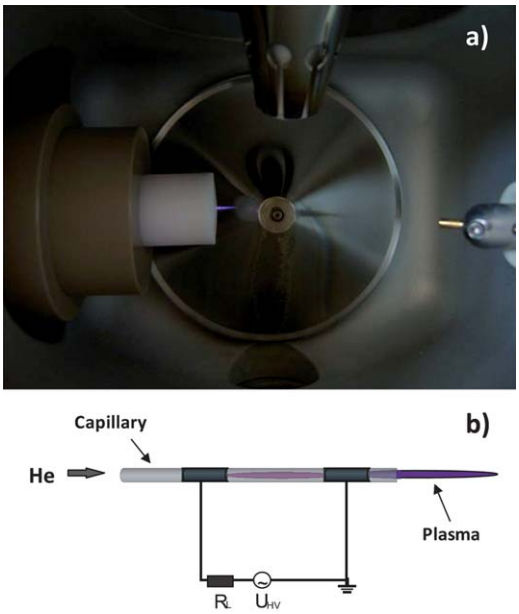

Fig. 1 (a) Positioning of the DBDI source (left) with respect to the MS inlet. (b) Schematic outline of the DBDI probe.

for ambient mass spectrometry is that here there are two dielectric layers 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 the electrode and to transport the gas, whereas the glass slide 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 plasma jet was located on the left side of the source housing, in the radial and not as previously in the axial position with respect to the MS inlet capillary (Fig. 1). This ion source, like the unmodified APCI source, works with a heated nebulizer maintained at 450 °C. 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 flow of nitrogen (sweep gas, flow rate of 2.0 arbitrary units) in 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).

Results and discussion

Ionization and mass spectral features of DBDI-MS

A suite of *ca.* 75 representative and highly relevant compounds was 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

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	Acenaphthylene	10.80	$[M]^+$	$C_{12}H_8$	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	$[M]^+$	$C_{13}H_{10}$	166.07770	166.07707	−3.8	10
9	Acenaphthene	11.88	$[M]^+$	$C_{12}H_{10}$	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	$[M]^+$	$C_{14}H_{10}$	178.07770	178.07760	−0.6	25
12	Anthracene	12.39	$[M]^+$	$C_{14}H_{10}$	178.07770	178.07756	−0.8	20
13	Fluoranthene	13.13	$[M]^+$	$C_{16}H_{10}$	202.07770	202.07758	−0.6	16
14	Pyrene	13.72	$[M]^+$	$C_{16}H_{10}$	202.07770	202.07759	−0.6	12.5
15	Benz[*a*]anthracene	14.70	$[M]^+$	$C_{18}H_{12}$	228.09335	228.09277	−2.6	6[a]
16	Chrysene							
17	Benzo[*b*]fluoranthene	16.49	$[M]^+$	$C_{20}H_{12}$	252.09335	252.09311	−1.0	10
18	Benzo[*k*]fluoranthene	16.73	$[M]^+$	$C_{20}H_{12}$	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	10
			$[M]^+$	$C_{20}H_{12}$	252.09335	252.09290	−1.8	
20	Hexachlorobenzene	18.00	$[M–Cl + O]^-$	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	10
			$[M]^+$	$C_{22}H_{14}$	278.10900	278.10851	−1.8	
22	Benzo[*ghi*]perylene	19.52	$[M + H]^+$	$C_{22}H_{13}$	277.10118	277.10054	−2.3	10
			$[M]^+$	$C_{22}H_{12}$	276.09335	276.09292	−1.6	
23	Indeno[1,2,3-*cd*] pyrene	19.90	$[M + H]^+$	$C_{22}H_{13}$	277.10118	277.10134	0.6	10
			$[M]^+$	$C_{22}H_{12}$	276.09335	276.09295	−1.5	

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

spectral features of the LC/DBDI-MS analysis of these compounds are summarized in Tables 1 and 2 (and Table S2, ESI†).

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 a 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 ($[M]^+$) 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 $[M]^+$. In the case of the non-polar compounds with low proton affinity (such as hexachlorobenzene, pentachlorobenzene or endosulfan sulfate), a different ionization pattern can be envisaged. While the organochlorine insecticide endosulfan sulfate exhibited

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

$[M - H]^-$ as the main peak, both hexachlorobenzene and pentachlorobenzene exchanged one chlorine atom with an oxygen ($[M–Cl + O]^-$).

In positive ion mode proton transfer is the dominating ionization mechanism, whereas in the negative ion mode several other mechanisms occur. Potential ionization mechanisms may include electron capture (EC), dissociative EC, and proton abstraction.[35,36] It should be highlighted that the relative signal intensity in the negative ionization mode is lower than in the positive ion mode. This could be attributed amongst other reasons to the fact that the standard mobile phase combination selected (water with formic acid and acetonitrile) is more suitable for positive ion formation.

Interestingly, the relative position of the DBDI probe with regard to the MS inlet (orifice) and HPLC outlet (APCI heater probe) seems to play an important role in the mass spectral features. In the previous study, using an axial positioning of the plasma jet (relative to the MS inlet), a wide array of oxidized species was observed in the mass spectra of PAHs.[23] In this study, the signal obtained by DBDI of PAHs was distributed among several others mainly based on oxygen addition. Adduct formation with acetonitrile was also observed with polar compounds such as amino acids. These phenomena constitute a disadvantage in terms of sensitivity and spectra interpretation for identification purposes. These ions were not detected with the orthogonal positioning of the plasma jet. The current source geometry configuration (see Fig. 1a) allowed obtaining simpler mass spectra in most cases. This provides significant sensitivity enhancement and a straightforward mass spectra interpretation.

Analytical performance of LC/DBDI-MS for the multiclass determination of organic contaminants in food and environment

Three examples were tested: multiclass organic contaminants in olive oil, priority and emerging contaminants in wastewater effluents and multiclass pesticides in orange. The latter application of LC/DBDI-MS analysis of pesticides in oranges as a non-fatty vegetable matrix will be described solely in the ESI.† The results obtained are analogous to the two other applications, but give additional support of the versatility of LC/DBDI-MS.

Multiclass detection of organic contaminants in virgin olive oil. There are some pesticides which are not ionized efficiently by ESI-based methods. This is the case of endosulfan sulfate, an insecticide ubiquitous in olive oil,[37] or hexachlorobenzene. Both compounds are not amenable to liquid chromatography coupled to atmospheric pressure ionization mass spectrometry (LC/API-MS). Only the use of direct electron ionization (EI) interface for LC/MS has been reported for the simultaneous detection of GC and LC amenable compounds in the same run without changes in the instrument performance.[5]

A detailed study by Thurman *et al.* reported that 1 μg of endosulfan injected on the column (40 μg mL^{-1}, 25 μL injected) gave no signal on ESI (+), ESI (−), APCI (+) or APCI (−) using a full-scan instrument.[38] Although successful analyses of endosulfan sulfate by LC/APCI-MS have been reported,[39,40] these methods cannot be used to detect endosulfan sulfate at reasonably low concentration levels without excessive sample preconcentration.[39,40]

The detection of PAHs in edible oils is also of great relevance, but they cannot be analyzed by LC/ESI-MS, thus requiring either a specific APCI, APPI, direct-EI or APLI method or GC/MS. In contrast, diuron and dimethoate are two agrochemicals used on olives – and frequently found in olive oil – that do not work well with GC/EI-MS. Therefore, the simultaneous analysis of these species cannot be straightforwardly accomplished by a unique technique. LC/DBDI-MS, however, was found to be very effective for their simultaneous analysis.

Fig. 2 shows an example of an olive oil extract spiked with 100 ng g^{-1} of the targeted contaminants. The olive oil sample was extracted using the QuEChERS method for fatty matrices. The final injected extract/sample ratio is 1 g mL^{-1} extract, the standard one in this type of analyses. The analysis was performed in polarity switching mode (10 Hz) using a resolving power of *ca.* 25 000 (0.4 s acquisition time for each ionization mode), so that all the results obtained (both positive and negative ionization mode) were collected in a single run (acquisition time of *ca.* 0.9 s for both ionization modes). The extracted ion chromatograms shown were reconstructed with a 20 ppm mass window width. At the 100 μg kg^{-1} level, all the tested species were detected. More than 20 compounds with different physicochemical properties were analyzed in one run. Note that all the EIC traces exhibited signal-to-noise ratios distinctly far from the limit of quantitation. Table 1 shows the retention time, elemental composition, and experimental mass error obtained in the measurement. Note that mass errors obtained were within 2 ppm (relative mass error) with external calibration in most cases regardless of the ionization mode. This relative low average mass error provides unambiguous identification of each targeted species. The limits of detection (LOD) obtained were in the range from 0.3 to 30 μg kg^{-1} depending on the analyte. With regard to the values obtained for pesticides in olive oil, the limits of detection were below or equal to 10 μg kg^{-1} for all studied pesticides. In the case of PAHs, LODs were below or equal to 20 μg kg^{-1} for almost all compounds studied. Only acenaphthylene, acenaphthene and phenanthrene showed higher LODs (25–30 μg kg^{-1}). Further improvement may be achieved by using a triple quadrupole analyzer in the multiple reaction monitoring mode, with a typical sensitivity increase of around one order of magnitude, depending on the instrument. The linearity of the method was studied by preparing matrix-matched standards across the range 10–400 μg kg^{-1}. Using the DBDI source correlation coefficients higher than 0.997 were obtained for all target analytes. The comparison of the calibration slopes obtained in solvent-based and in matrix-matched standards revealed minor signal enhancement or suppression, lower than 20% (slope ratios typically in the range 0.8–1.2) in most cases, which is generally not considered significant. These results (see detailed data in Table S1 in the ESI†) are remarkable in such a complex fatty matrix. This example of multiclass multipolarity detection of organic contaminants in olive oil shows the versatility and potential of the ionization source for a wide array of different compounds in complex samples.

Simultaneous multiclass detection of priority and emerging organic contaminants in effluent wastewater. The proposed approach for multiclass widescope screening was also evaluated for a demanding application such as effluent wastewater.

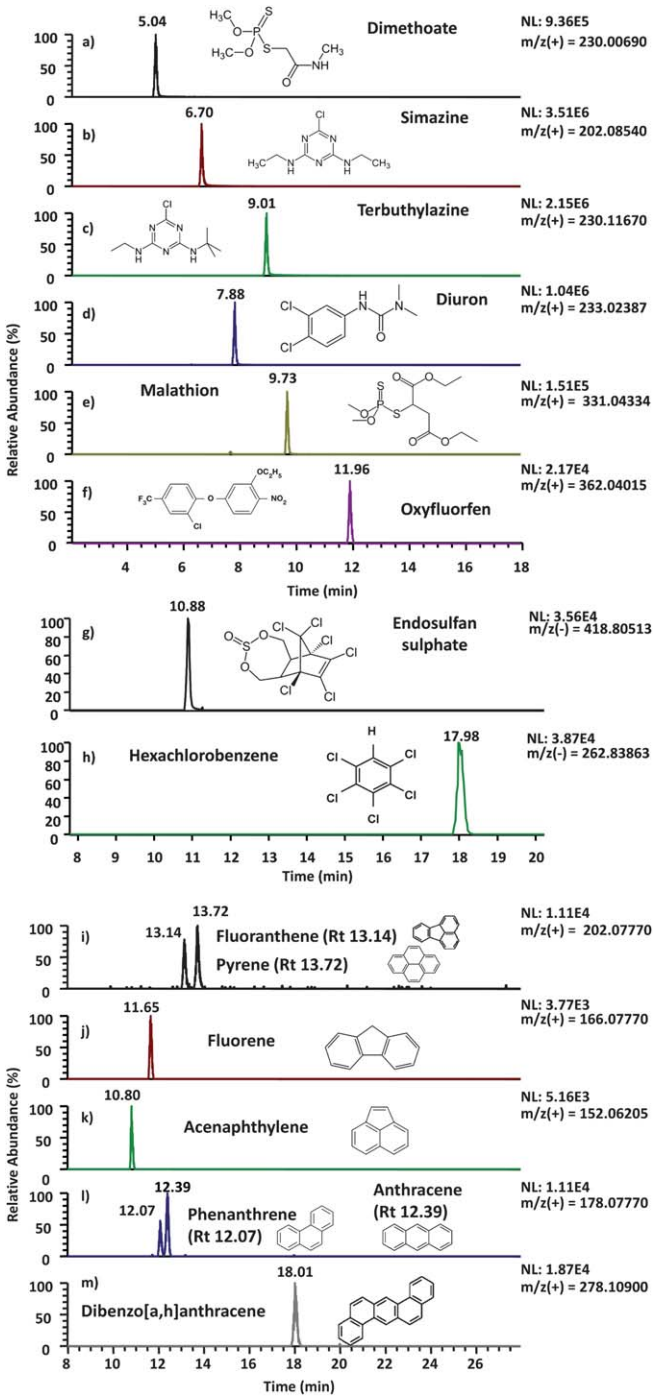

Fig. 2 LC/DBDI-MS analysis in polarity switching ionization mode of an olive oil extract spiked at 100 ng g^{-1} (each) with a mixture of pesticides and PAHs. EICs corresponding to the following selected compounds: (a) dimethoate, (b) simazine, (c) terbuthylazine, (d) diuron, (e) malathion, (f) oxyfluorfen,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

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

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 the DBDI and APCI sources. 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 compares well against the standard LC/MS ionization methods. The DBDI ionization coverage falls in-between APCI and ESI, showing 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

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

				DBDI *vs.* APCI([a])	DBDI *vs.* ESI([b])	
	Compound	Rt	Polarity	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/	14.70	+	0.7	6[d]	—[e]
7	Chrysene					
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 the 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[41] did not yield any signal for the mentioned analytes, which are considered elsewhere as non-electrospray amenable.

performance that DBDI offers for relatively polar species, which often display $[M + Na]^+$ adducts in ESI, such as most 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 (and thus more nonpolar) PAHs. 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 a 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 modes 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 the 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 has required until 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 be carried out in the future.

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