Direct Probe Atmospheric Pressure Photoionization /Atmospheric Pressure Chemical Ionization High Resolution Mass Spectrometry for Fast Screening of Flame Retardants and Plasticizers in Products and Waste

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Abstract

In this study we develop fast screening methods for flame retardants and plasticizers in products and waste based on direct probe (DP)-atmospheric pressure photoionization (APPI) and atmospheric pressure chemical ionization (APCI) coupled to a high resolution time-of-flight mass spectrometer (HR-TOF-MS). DP-APPI is reported for the first time in this study and DP-APCI, that has been scarcely exploited, is optimized for comparison. DP-APPI was more selective than DP-APCI and also more sensitive for the most hydrophobic compounds. No sample treatment was necessary and only a minimal amount of sample (few milligrams) was used for analysis that was performed within a few minutes. Both methods were applied to the analysis of plastic products, electronic waste and car interiors. Polybrominated diphenylethers (PBDEs), new brominated flame retardants (BFRs) and organophosphorus flame retardants (PFRs) were present in most of the samples. The combination of DP with HR mass spectra and data processing based on mass accuracy and isotopic patterns allowed the unambiguous identification of chemicals at low levels of about 0.025 % w/w. Under untargeted screening, resorcinol bis(biphenylphosphate) (PBDPP) and bisphenol A bis(bisphenylphosphate) (BPA-BDPP) were identified in many of the consumer products of which literature data is still very limited.

KEYWORDS: direct probe; ambient mass spectrometry; atmospheric pressure chemical ionization; atmospheric pressure photoionization; flame retardants

1. Introduction

Sample preparation is still the bottleneck in analytical procedures for environmental, food and biological analysis. Despite the numerous advances in miniaturization and on-line procedures, the need of multiple steps and a large consumption of toxic organic solvents make the analysis laborious, time-consuming and expensive. Ambient mass spectrometry (MS) techniques have emerged during the last years as an alternative for developing rapid screening methods providing high sensitivity, throughput and elucidation capacity of molecular structures.

Ambient MS is based on new ion sources capable of desorbing the analytes directly from the sample with minimal or no sample treatment and of ionizing chemicals under ambient conditions. Since the introduction of desorption electrospray ionization (DESI) at the end of 2004 [1] and direct analysis in real time (DART) in 2005 [2], variations of these ionization techniques have been developed to broaden the field of applications or fulfilling some specific analytical needs, such as easy sonic spray ionization (EASI) [3,4] and extractive electrospray ionization (EESI) [5,6]. In DESI and DART, a sample surface is ionized by directing charged droplets produced from a pneumatically-assisted electrospray or by a stream of excited helium atoms that produce ionized atmospheric gases (such as water vapor and oxygen). In electrospray-assisted laser desorption/ionization (ELDI) [7] the sample is first irradiated by laser close to the ESI plume, wherein the neutrals are then ionized, thus facilitating desorption from hard surfaces. DESI, DART, ELDI and analogues ambient MS techniques are highly suitable for quality control processes and have been applied in drug discovery, doping control, forensic identification and food safety [reviewed in 8-12], including applications for in-vivo analysis [13,14] and imaging techniques [15,16].

On the other hand, and with the aim of extending the applicability of ambient MS to less polar compounds (being this the case of PBDEs and new BFRs) desorption atmospheric pressure chemical ionization (DAPCI) [17,18] and desorption atmospheric pressure photoionization (DAPPI) have been reported [19]. A simpler variant of DAPCI is the so-called atmospheric pressure solids analysis probe (ASAP), first reported in 2005 [20], in which the sample is placed within the source vaporizer gas (usually hot nitrogen) so that the desorption/ionization takes place without any additional desorption spray. ASAP has been applied to food analysis [21], polymer materials [22,23] and biological [24,25] and environmental [26] samples.

Flame retardants are frequently applied in electronics, clothes and furniture for enhancing fire safety. Due to their persistence and toxic properties [28,29] authorities have restricted the use of PBDEs with a maximum concentration of 0.1 % by weight in electronic and electrical equipment. Screening methods proposed in literature for flame retardants include laser-induced plasma spectroscopy (LIPS) [30], total-reflection X-ray fluorescence spectroscopy (TXRF) [31] and radiofrequency glow discharge (rf-GD) coupled to optical emission spectrometry (OES) [32] or MS [33]. These are all based on total bromine content. The DP methods we describe constitute a good alternative by offering the possibility to identify the individual flame retardants including those without bromine. The direct probe is based on a similar principle as ASAP when operating in APCI mode but with a different assembly configuration. The potential of direct probe (DP)-HRTOF-MS with an APCI source for screening flame retardants was recently and briefly discussed by our group and applied to four waste samples [34] without further optimisation or validation. On the other hand, DP-HRTOF-MS with an APPI source is in this study proposed for first time as analytical technique. The present study describes the optimisation, validation and comparison of DP-APCI and DP-APPI methods for a wide variety of flame retardants and

plasticizers in plastic products and waste. DP-APPI provided a better selectivity and was also more sensitive for the most apolar flame retardants, so proposed as optimal method. The use of a screening software based of mass accuracy and isotopic patterns allowed the unambiguous identification of contaminants at low levels required for compliance of legislation (below ~0.025 percentage in weight).

2. Experimental section

2.1. Chemicals and reagents

Information about chemicals and suppliers is provided in the Supplementary Data (SD) of this article. The abbreviation system for flame retardants and plasticizers recently proposed by Bergman et al. [35] were used. A number of standards of flame retardants and plasticizers were used for studying the main ions formed in DP-APCI/APPI sources and making a list of target ions for targeted screening analysis. The list of flame retardants studied in targeted and untargeted screening is given in the Tables S-2 and S-3 of Supplementary Data (SD). These compounds were new BFRs, namely tetrabromobisphenol A (TBBPA); α-, β-, and δ-hexabromocyclodecane (HBCD); allyl 2,4,6-tribromophenyl ether (ATE); 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE); bis(2-ethyl-1-hexyl)tetrabromophtalate (BEHTBP); decabromodiphenylethane (DBDPE); 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE); hexachlorocyclopentenyl-dibromocyclooctane (HCDBCO); 2-ethylexyl-2,3,4,5-tetrabromobenzoate (EHTBB), 2-bromoallyl 2,4,6-tribromophenyl ether (BATE) and the PFRs, including tris(butyl) phosphate (TNBP); tris(isobutyl) phosphate (TiBP); tris(2-chloroisopropyl) phosphate (TCIPP); tris(2-butoxyethyl) phosphate (TBOEP); 2-ethylhexyldiphenyl phosphate (EHDP); 2-Ethylhexyl phosphate (TEHP) and tris(phenyl) phosphate (TPHP); tris(1,3-

dichloroisopropyl) phosphate (TDCiPP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), tris(methylphenyl) phosphate (TMPP) and) and 3,4:5,6-dibenzo-2H-1,2-oxaphosphorin-2-oxide (DOPO).

2.2. Instrumentation

A microTOF II mass spectrometer (Bruker Daltonics, Bremen, Germany; mass accuracy <2ppm and resolution >16,500 FWHM) equipped with either APCI or APPI sources and with a direct probe assembly, was employed.

The DP provided by Brukers Daltonics is a minor modification of a standard APCI or APPI source. Differently from ASAP in which the probe is introduced laterally into the source, the probe is mounted instead of a nebulizer sprayer on top of the vaporizer heater of the APCI/APPI source. The nebulizer gas is directly connected to the DP and directed against it. A sketch is shown in Figure 1. For the calibration of the DP-APCI and DP-APPI sources, an external calibration before each run of experiments (few hours) was not enough to assure mass accuracy within acceptable levels. Therefore, we introduced the calibration solution in each run by adding a small droplet of calibration solution (~5 µL) directly onto the probe after the collection of the sample. DP-APCI/APPI MS parameters are given in Table 1. For confirmation purposes, extraction and analysis of electronic waste and car interiors was performed by GC-APCI-HRTOF-MS as described before by our research group [34] and by GC-electron capture chemical ionization (ECNI)-MS or GC-electron ionization (EI)-MS for plastic consumer products (see Supplementary Data). The software data analysis 4.0 from Bruker Daltonics (Bremen, Germany) was used for screening by *smart formula* and *compound crawler* tools. *Smart formula* provides identification on the basis of accurate mass and isotopic pattern.

130 *Compound crawler* connects with online accurate mass databases (e.g. Metlin, Chemspider) for
131 formula identification in untargeted screening.

132 **2.3. Sample analysis**

133 Samples of car interiors (*n*=10) and electronic waste (e-waste, *n*=2) from recycling plants were
134 kindly supplied by the Flemish Institute for Technological Research (VITO, Antwerp, Belgium)
135 as shredder material (less than ~1 mm particle size). A variety of hard plastic parts of consumer
136 products (electrical adaptors a power board, televisions and a plastic adorn, *n*=9) were also
137 analyzed as supplied. No sample preparation was required.

138 The glass probes were loaded (in the open side of the tube) with a tiny amount of sample (few
139 milligrams) by inserting them directly into the shredder material (car interiors and e-waste) or by
140 scratching the surface of the solid sample (consumer products) with the probe to release small
141 particles. The size of sample particles for DP analysis should be in the micrometer range to
142 obtain an efficient desorption/ionization. This can easily be obtained by scratching the surface of
143 the material. Main particles in the outer surface of the probe were removed with a lint-free cotton
144 cloth to prevent contamination of the source and a drop of ~5 µL of calibration solution was
145 added at the outer surface of the probe before introducing it into the MS source.

146 After each run (3-4 min), the probe was removed and the vaporization source temperature
147 increased to 450 ºC (~2 min) for cleaning possible residues. Blanks (unloaded probes with
148 calibration solution) were checked between samples to prevent carry-over contamination. The
149 MS parameters for analysis are given in Table 1.

Data processing was done by *smart formula* tool of *data analysis* software in order to obtain mSigma values (match factor between the measured isotopic pattern and the theoretical pattern for a given formula) and mass accuracy values for confirmation of the analytes. Some parameters, such as the number of bromine or chlorine atoms or even a complete molecular formula (when studying a list of compounds for targeted screening, e.g. see Tables 1 and 2 of SI), can be introduced in the tool to generate the most probable *match*. General parameters for formulae generation were as follows: mass error tolerance was set at 5 ppm; H/C ratio from 0 to 3; number of rings and double bonds were restricted to 0.5-40. The option *automatically detect isotopic mass* was activated. Values of < 5 ppm of mass error and <100 of mSigma were considered acceptable for positive confirmation (mSigma <100 acceptable, <50 good and <25 excellent).

3. Results and discussion

3.1. HR-TOF-MS parameters optimization

Experiments were made by adding a drop (~5 µL) of a concentrated standard solution of the target compounds (0.5 µg mL^{-1}) directly into the probe. The same major ions were observed in both APCI and APPI sources. For BFRs analyzed in the negative mode, $[M-Br+O]^-$ was the main ion, except for TBBPA and HBCD ($[M-H]^-$), BTBPE (fragment $C_6Br_3H_2O^-$) and HCDBCO ($[M-Cl+O]^-$). For PFRs analyzed in the positive mode, the main ion observed was $[M+H]^+$, except for EHDP $[M-C_8H_{17}+H_2]^+$. In the case of TBBPA, the $[M-Br+O]^-$ ion had the same intensity as the $[M-H]^-$ ion in the APCI (-) and with about a 5-fold lower intensity in APPI (-). Target ions with accurate mass values of the flame retardants and plasticizers included in this study are given in Table 1 and 2 of the Supplementary Data.

The MS parameters capillary exit and skimmer 1, hexapole RF, transfer time and pulse storage time also have a strong influence on the sensitivity and selectivity and can be tuned in function of the *m/z* range of interest. A compromise was selected as optimal for the mass range of interest 200-1000 *m/z*. (see Table 1).

For sample analysis the instrument was operated in the highest resolution mode (*option focus on)* and was necessary to provide a good separation between the main ions of TCIPP (327.0081) and of TPHP (327.0781).

In general, the APPI source generated cleaner spectra than the APCI source at the same temperature (more selective ionization mechanism) and, as expected, a better sensitivity for highly apolar compounds, e.g. for DBDPE the signal was around 2-3 times higher in APPI than APCI mode (when operating at optimal conditions in each source).

3.2. APCI/APPI source parameters optimization

The vaporizer temperature, APCI corona voltage and the possibility of introducing a dopant solvent were studied in a sample of e-waste containing a variety of PBDEs (sample e-waste 1) and TBBPA, a consumer product sample (power board) containing PBDPP and BPA-BDPP, both analyzed in the negative mode, and a car interior sample (car interior 2) containing TCIPP in the positive mode.

3.2.1. Vaporizer temperature

The source temperature is a key parameter in ambient desorption experiments, being together with the corona discharge in APCI and the UV irradiation in APPI, the major contributors to the ionization yield. The vaporizer temperature is a heated, insulated ceramic tube, which evaporates

193 the mobile phase or, in the case of the direct probe, desorbs the compounds directly from the
194 solid trough thermal radiation. This parameter strongly influenced the sensitivity of the method
195 and was optimized.

196 In general, high temperatures are set for ASAP experiments (ramps between 100-400 ºC for
197 low molecular weight compounds and 400-650 ºC for polymers). The vaporizer temperature was
198 tested between 175 and 375 ºC. For flame retardants in solution, temperatures around 200-225 ºC
199 were high enough for ionization of every analyte in the APCI and APPI mode, while higher
200 temperatures were required to allow their desorption/ionization from solid material, especially
201 for the less volatile compounds, i.e. BDE 209 (4.0E-8 Pa vapor pressure), DBDPE (2.31E-16
202 Pa), PBDPP (5.01E-11 Pa) and BPA-BDPP (1.97E-15 Pa).

203 At the highest temperatures tested (350-375 ºC), the desorption/ionization was very fast and
204 the signal-in-time too short (few seconds) for the analytes present at low concentrations. This
205 made the screening very difficult, especially in APCI mode. Furthermore, the matrix noise
206 increased with increasing temperature, thus making the spectra less clear for identification. So,
207 the minimal temperature giving maximal intensity was considered as optimal.

208 In DP-APCI, desorption-ionization of target compounds started at 175-200 ºC and
209 temperatures around 250 ºC gave already a maximum sensitivity for most of the compounds,
210 while for PBDPP and BPA-BDPP, the optimum was found at 275 ºC. In the case of BDE 209 in
211 e-waste samples, values of 200-225 ºC, although detrimental for the sensitivity, were preferred,
212 because at higher temperatures an increase in the background noise in the *m/z* region of interest
213 was observed (see Figure 2) that hampered the identification.

In the APPI source, higher temperatures were required for efficient desorption/ionization, i.e. around 250 ºC was optimal for PFRs and TBBPA, 300-310 ºC for BFRs (including BDE 209) and 325-350 ºC for PBDPP and BPA-BDPP.

Figure 2 shows the spectra for sample e-waste 1 at different temperatures with DP-APCI(-)/APPI(-)-HRTOF-MS. Due to the different optimum temperatures for the different flame retardants and in order to obtain a certain degree of separation between matrix components and target compounds, two vaporizer temperature segments were set in the program of the analysis, namely at 210 ºC (0-1.5 min) and 280 ºC (1.5-3 min) in APCI (-); at 250 ºC (0-1.5 min) and 300 ºC (1.5-3 min) in APCI (+); at 250 ºC (0-1.5 min) and 300 ºC (1.5-3 min) in APPI(-) and at 250 ºC (0-1.5 min) and 325 ºC (1.5-3 min) in APPI (+).

3.2.2. APCI corona voltage

Regarding the corona voltage in APCI, increasing values caused an increase in intensity and these were also analyte-dependent (the lower polarity compounds being more affected). High corona voltage values also caused an increase in background noise, making the identification more difficult, so minimal values giving acceptable intensities for target ions were considered as optimal. A value of 5000 nA was selected as optimum for the positive mode. In the negative mode, values higher than 6000 nA were necessary for the desorption/ionization of nona- and BDE 209, with 8000 nA as optimum to assure efficient ionization.

3.2.3 APPI dopant solvent

Although not provided by the instrument supplier, we introduced and optimized the use of a dopant solvent into the source for increasing sensitivity (and applicability) trough indirect APPI.

Indirect APPI is necessary for compounds without a UV chromophore and can increase the sensitivity of those containing chromophore groups. Toluene, a dopant used in the literature for the analysis of flame retardants with APPI [36], was introduced into the source by a syringe pump (0-130 µL min^{-1}) through an additional gas port. E-waste sample 1 and car interior sample 2 were analyzed at 200 ºC, 300 ºC and 350 ºC. The signal intensity of the target compounds TBBPA, hepta-BDE and BDE 209 in the negative mode and TCIPP in the positive mode in e-waste 1 and car interior 2 were studied. At low temperatures (200 ºC) and by increasing the dopant flow, the signals of all analytes increased from 0 to 100 µL min^{-1} with a factor of 1.9, 2.0, 4.3 and 5.8 for TBBPA, hepta-BDE congeners, BDE 209 and TCIPP, respectively, and were then constant until 133 µL min^{-1}. However, at temperatures above 300 ºC there was no further improvement in sensitivity by the presence of the dopant. At this point the temperature and the UV radiation were sufficient for an efficient desorption/ionization. This simpler direct APPI option was finally selected for the analysis of the samples, although working at lower temperatures with dopant-APPI provides cleaner spectra and could be a valuable modification for the commercialized DP-APPI source in the analysis of complex matrices.

The spectra of the consumer product sample (power board) at 200 ºC, with and without dopant and at 300 ºC without dopant APPI (-) and at 200 ºC in APCI (-) are shown in Figure S-1 (SD). Similar results are obtained in indirect APPI (200 ºC, with dopant), direct APPI (300 ºC) and APCI (200 ºC) with DBDPE ca. 2-fold more sensitive in the APPI mode.

3.3. Sample analysis

3.3.1. Targeted screening and validation of results by a secondary technique

Samples of electronic waste, consumer products and car interiors were analyzed with DP-APCI and DP-APPI and the compounds were identified with the *smart formula* tool. Tables 2 and 3 show the results of the targeted screening and the quantitation and or confirmation values by a standard analysis method (confirmatory technique). Values <5 ppm error and <100 mSigma were considered acceptable. DP-APPI was found advantageous in terms of selectivity and sensitivity. Although we could confirm the presence of the compounds with both APPI and APCI, the APPI spectra were cleaner due to the higher selectivity of this source, which is interesting for future applications to more complex samples. The signal of the most hydrophobic compounds, BDE 209, DBDPE and BPA-BDPP were around 2-3 times higher in the APPI mode.

Regarding the reproducibility of the method, seven aliquots of e-waste 1 and of the adaptor 2 samples were analyzed by DP-APPI and DP-APCI and the compounds confirmed in all of them. As an example and when using DP-APPI, the main ion of TBBPA in the sample e-waste 1 was confirmed with values of mass error, mSigma (isotopic pattern) and intensity (total ion current) in the ranges of 0.4-5.0, 40-100 and 150000-200000, respectively. For the main ion of TPHP in the sample adaptor 2, the values of mass error, mSigma and intensity were in the ranges of -1.2-3.8, 0.6-10 and 200000-400000, respectively. On the basis of this results we can conclude that the method was reproducible and that the content of flame retardants was homogenous enough for a reproducible analysis by using only few milligrams of sample.

278 In general, when operating in the negative ionization mode, highly brominated PBDEs,
279 TBBPA and BTBPE were the most frequently detected compounds in both e-waste and plastic
280 consumer products. No BFRs were detected in car interior samples. TPHP was the most common
281 PFR in e-waste and consumer products (only not found in one TV sample), while in samples of
282 car interiors (results not included in the tables) only TCIPP was present at levels high enough for
283 detection with the direct probe (>100 µg g^{-1}). The results were later confirmed by GC-APCI(+)-
284 HR-TOF-MS analysis. TMPP was detected in one e-waste sample, one television sample and a
285 plastic adorn. TCEP was detected in one LCD television.

286 For a limited number of results we found some discrepancy between the DP analysis and the
287 confirmatory techniques. A false positive for DP analysis was for example found for BTBPE in
288 the power board and TV 1 sample. The main ion of BTBPE is less selective since it is a fragment
289 $[C_6Br_3H_2O]^-$ and various other brominated molecules can also produce it. Six different isomers
290 of tribromophenol or 2,5-cyclohexadien-1-one, 2,6-dibromo-4-(bromoimino) (CAS No 64693-
291 24-9) can cause this interference if the parent ion is [M-H] and four isomers of dibromo-p-
292 benzoquinone (CAS No 1633-14-3) and 3,4-dibromo-5-ethynyl-2(5H)-furanone (CAS No
293 149418-41-7) can cause the same problem if $[M-Br+O]^-$ is the parent ion. In fact, when these
294 samples were analyzed with gas chromatographic separation prior to MS detection, we observed
295 different peaks at different retention times with this same fragment as major ion.

296 On the other hand, DBPDE, a substituent of BDE 209 was detected with DP only in the power
297 board sample and in the TV 1 sample, while by using GC-ECNI-MS it was found in all of the
298 nine plastic products. A possible interference, since the non-selective bromine fragment (*m/z* 79,
299 81) was used for identification with GC-ECNI-MS, or the need of further optimization of DP
300 methods for DBDPE for some matrices are possible explanations.

The quantitative values obtained by GC-MS were used to estimate the LOD of the method as the minimal quantitative amount of target compounds measured by GC-MS that could be also confirmed by direct probe analysis. LODs were based on ion signals with S/N above 10 (values provided by Data Analysis program) for an averaged spectra of about 0.5 min, together with acceptable mass error and mSigma screening values. A general detection limit of about 0.25% w/w was estimated in this way based on the GC-MS data available. Figure S-2 shows the spectra of TPHP at two concentration levels (1.6 and 14.4 times higher than the LOD).

3.3.2. Untargeted screening. Identification of novel flame retardants

Since, DP-APPI provided better sensitivity and selectivity than DP-APCI we applied it for the untargeted screening of the samples. Two novel PFRs, PBDPP, BPA-BDPP, for which data is scarce in the literature, were identified in many of the consumer products. They have been recently reported in polymers [37] and dust samples [38]. In this case, the DP-APPI analysis is clearly advantageous for the analysis of these heavy and low volatile molecules since any sample treatment or chromatographic separation that could hamper the subsequent detection is avoided. PBDPP and BPA-BDPP can be used as a substitute for BDE 209 in TV/flat screen housings and other electronic consumer products [39]. They are used in a variety of polymers; PBDPP is used in acrylonitrile butadiene styrene (ABS), polycarbonate (PC)/ABS, poly(p-phenylene) oxide (PPO)/ high impact polystyrene (HIPS) and BPA-BDPP in HIPS, PC, PPO and PC/ABS [32]. This could explain the detection in many products. The identification of these new flame retardants when performing untargeted screening by DP-APPI(+) is shown in Table 4. Figure 3 shows the whole spectra of the power board sample by DP-APPI(+) together with the spectra of PBDPP and BPA-BDPP this sample. These findings highlight the need for the development of wide screening tools, such as the ones proposed here, for hitherto unknown flame retardants.

4. Conclusions

Ambient MS techniques based on DP-APPI (and DP-APCI) coupled to HR-TOF-MS have successfully been applied for the fast screening of flame retardants with detection limits of about 0.025 % w/w. The DP-APPI-HRTOF-MS method is reported for the first time and showed better selectivity and sensitivity for highly apolar compounds than DP-APCI. A variety of PBDEs, new BFRs and PFRs/plasticizers, including the novel PBDPP and BPA-BDPP by using DP-APPI, have been detected in samples of electronic waste, car interiors and consumer products and confirmed on the basis of mass accuracy and isotopic patterns. The results were confirmed by GC-ECNI-MS or GC-APCI(-)-HR-TOF. The DP-APPI/APCI-HR-TOF-MS methods are fast (few minutes), easy, inexpensive and provide with a broad scope screening for the identification of flame retardants for compliance with the European WEEE directive.

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Figure captions

Figure 1. Sketch of the direct probe.

Figure 2. DP-APCI(-)/APPI(-) spectra of E-waste sample 1 at different source vaporization temperatures. In the APCI mode at 250 ºC, the spectrum of the unidentified BDE 209 in these conditions is included as an insert.

Figure 3. DP-APPI(+) spectrum (A) of the power board sample at *m/z* 200-1200, (B) PBDPP spectrum, (C) BPA-BDPP spectrum.

Table 1. MS-HRTOF parameters

System	[1]TOF parameters
Direct Probe-APCI-HRTOF	Capillary (neg./pos.) -/+1000 V
	End plate offset (neg.) -1000 (pos.) -500
	Corona (neg.) -8000 nA (pos.) +5000 nA
	Dry gas 2 L/min
	Nebulizer 4 bar
	Dry Heater 220 °C
	Vaporizer temperature at 210 ºC (0-1.5 min) and at 280 ºC (1.5-3 min) in APCI (-) and at 250 ºC (0-1.5 min) and at 300 ºC (1.5-3 min) in APCI (+)
Direct Probe-APPI-HRTOF	Capillary (neg./pos.) -/+700 V
	End plate offset (neg.) -1000 (pos.) -500
	Dry gas 4 L/min
	Nebulizer 3 bar
	Dry Heater 220 °C
	Vaporizer temperature at 250 ºC (0-1.5 min) and 300 ºC (1.5-3 min) in APPI(-) and at 250 ºC (0-1.5 min) and 325 ºC (1.5-3.0 min) in APPI (+)

[1]TOF detection parameters: capillary exit: ±80 V; Skimmer1: ±26.7 V; Hexapole RF: 250 V (negative mode) and 200 V (positive mode); transfer time: 50; pulse. storage time: 10; focus on

Table 2. Presence of flame retardants in e-waste and consumer products analyzed by DP-APCI/APPI(-)HRTOF-MS and concentrations determined by a confirmatory technique[a,b] in parenthesis.

	HexaBDE	HeptaBDE	OctaBDE	NonaBDE	DecaBDE	TBBPA	BTBPE
E-waste 1	+ ([a]159 μg g^{-1})	+ ([a]1224 μg g^{-1})	+ ([a]675 μg g^{-1})	+ ([a]886 μg g^{-1})	+ ([a]1855 μg g^{-1})	+ ([a]16232 μg g^{-1})	+ ([a]1689 μg g^{-1})
E-waste 2	- ([a]12.9 μg g-^{1})	- ([a]80 μg g^{-1})	- ([a]29 μg g^{-1})	- ([a]30 μg g^{-1})	- ([a]71 μg g^{-1})	+ ([a]71 μg g^{-1})	- ([a]41 μg g^{-1})
Adaptor 1	- ([a]n.d.)	+ ([b]245 μg g^{-1})	+ ([b]150 μg g^{-1})	+ (n.a.)	+ ([b]8,100 μg g^{-1})	+ ([b]60,000 μg g^{-1})	+ ([b]590 μg g^{-1})
Adaptor 2	- ([b]30 μg g^{-1})	+ ([b]2,470 μg g^{-1})	+ ([b]1,510 μg g^{-1})	+ ([b]n.a.)	+ ([b]18,000 μg g^{-1})	+ ([b]68,500 μg g^{-1})	+ ([b]3,700 μg g^{-1})
Heat sealer	- ([b]n.d.)	+ ([b]1,700)	+ ([b]1,010 μg g^{-1})	+ ([b]n.a.)	+ ([b]5,050 μg g^{-1})	+ ([b]70,000 μg g^{-1})	+ ([b]2,600 μg g^{-1})
Power board	- ([b]n.d.)	- ([b]n.d.)	- ([b]n.d.)	- ([b]n.a.)	+ ([b]2,700 μg g^{-1})	+ ([b]70,200 μg g^{-1})	+ ([b]n.d.)
LCD TV 1	- ([b]30 μg g^{-1})	+ ([b]110 μg g^{-1})	+ ([b]110 μg g^{-1})	+ ([b]n.a.)	+ ([b]47,700 μg g^{-1})	+ ([b]1,520 μg g^{-1})	+ ([b]190 μg g^{-1})
LCD TV 2	- ([b]n.d.)	+ [b]400 μg g^{-1}	+ [b]385 μg g^{-1}	+ ([b]n.a.)	+ ([b]88,600 μg g^{-1})	+ ([b]2,500 μg g^{-1})	+ ([b]660 μg g^{-1})
TV 1	- ([b]n.d.)	- ([b]n.d.)	- ([b]n.d.)	- ([b]n.a.)	- ([b]11 μg g^{-1})	- ([b]n.d.)	+ ([b]n.d.)
TV 2	- ([b]n.d.)	+ ([b]2,470 μg g^{-1})	+ ([b]1,510 μg g^{-1})	+ ([b]n.a.)	+ ([b]1,510 μg g^{-1})	+ ([b]68,500μg g^{-1})	+ ([b]3,700μg g^{-1})
Plastic ornament	- ([b]n.d.)	+ ([b]260 μg g^{-1})	+ ([b]240 μg g^{-1})	+ ([b]n.a.)	+ ([b]70,000 μg g^{-1})	+ ([b]3,700 μg g^{-1})	+ ([b]430 μg g^{-1})

Analytical techniques used for validation of results: [a]GC-APCI(-)-HRTOF; [b]GC-ECNI-MS; n.d. non detected; n.a. non analyzed

Table 3. Presence of phosphorous flame retardants and plasticizers in e-waste and consumer products analyzed by DP-APCI/APPI(+)HRTOF-MS and concentrations determined by a confirmatory technique[a,b] in parenthesis.

	TCEP	TCIPP	TPHP	TMPP
E-waste 1	- ([a]0.81 μg g^{-1})	- ([a]n.d.)	+ ([a]3636 μg g^{-1})	+ ([a]1822 μg g^{-1})
E-waste 2	- ([a]1.51 μg g^{-1})	- ([a]n.d.)	+ ([a]591 μg g^{-1})	- ([a]12 μg g^{-1})
Adaptor 1	- ([b]n.d.)	- ([b]n.d.)	+ ([b]140 μg g^{-1})	- ([b]n.d.)
Adaptor 2	- ([b]n.d.)	- ([b]n.d.)	+ ([b]390 μg g^{-1})	- ([b]n.d.)
Heat sealer	- ([b]n.d.)	- ([b]n.d.)	+ ([b]330 μg g^{-1})	- ([b]n.d.)
Power board	- ([b]n.d.)	- ([b]n.d.)	+ ([b]n.d.)	- ([b]n.d.)
LCD TV 1	- ([b]n.d.)	- ([b]n.d.)	+ ([b]10,500 μg g^{-1})	- ([b]n.d.)
LCD TV 2	+ ([b]1,230 μg g^{-1})	- ([b]n.d.).	+ ([b]3,600 μg g^{-1})	- ([b]n.d.)
TV 1	- ([b]n.d.)	- ([b]n.d.)	- ([b]n.d.)	- ([b]n.d.)
TV 2	- ([b]n.d.)	- ([b]n.d.)	+ ([b]3,600 μg g^{-1})	+ ([b]220 μg g^{-1})
Plastic ornament	- ([b]n.d.)	- ([b]n.d.)	+ ([b]880 μg g^{-1})	+ ([b]90 μg g^{-1})

Analytical techniques used for validation of results: [a]GC-APCI(+)-HRTOF; [b]GC-EI-MS; -non detected; n.a. non analyzed

Table 4. Identification of flame retardants and plasticizers in e-waste and consumer products after untargeted screening by DP-APPI(+)HRTOF-MS with mass accuracy/mSigma (isotopic patterns fit) values.

	PBDPP	BPA-BDPP
E-waste 1	n.d.	n.d.
E-waste 2	n.d.	n.d.
Adaptor 1	4.0/35	-1.4/47
Adaptor 2	3.1/32	2.0/21
Heat sealer	3.8/7	1.7/14
Power board	0.7/19	-2.5/12
LCD TV 1	-0.2/56	-0.3/4
LCD TV 1	0.4/24	-0.7/15
TV 1	n.d.	n.d.
TV 2	n.d.	n.d.
Plastic ornament	1.2/17	-3.5/7

n.d.: non detected

Figure 1

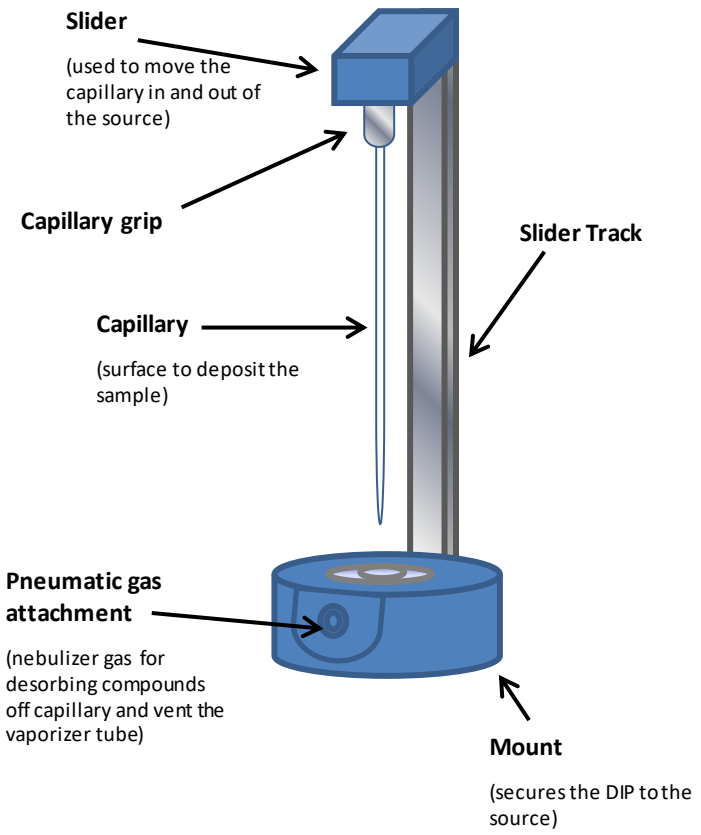
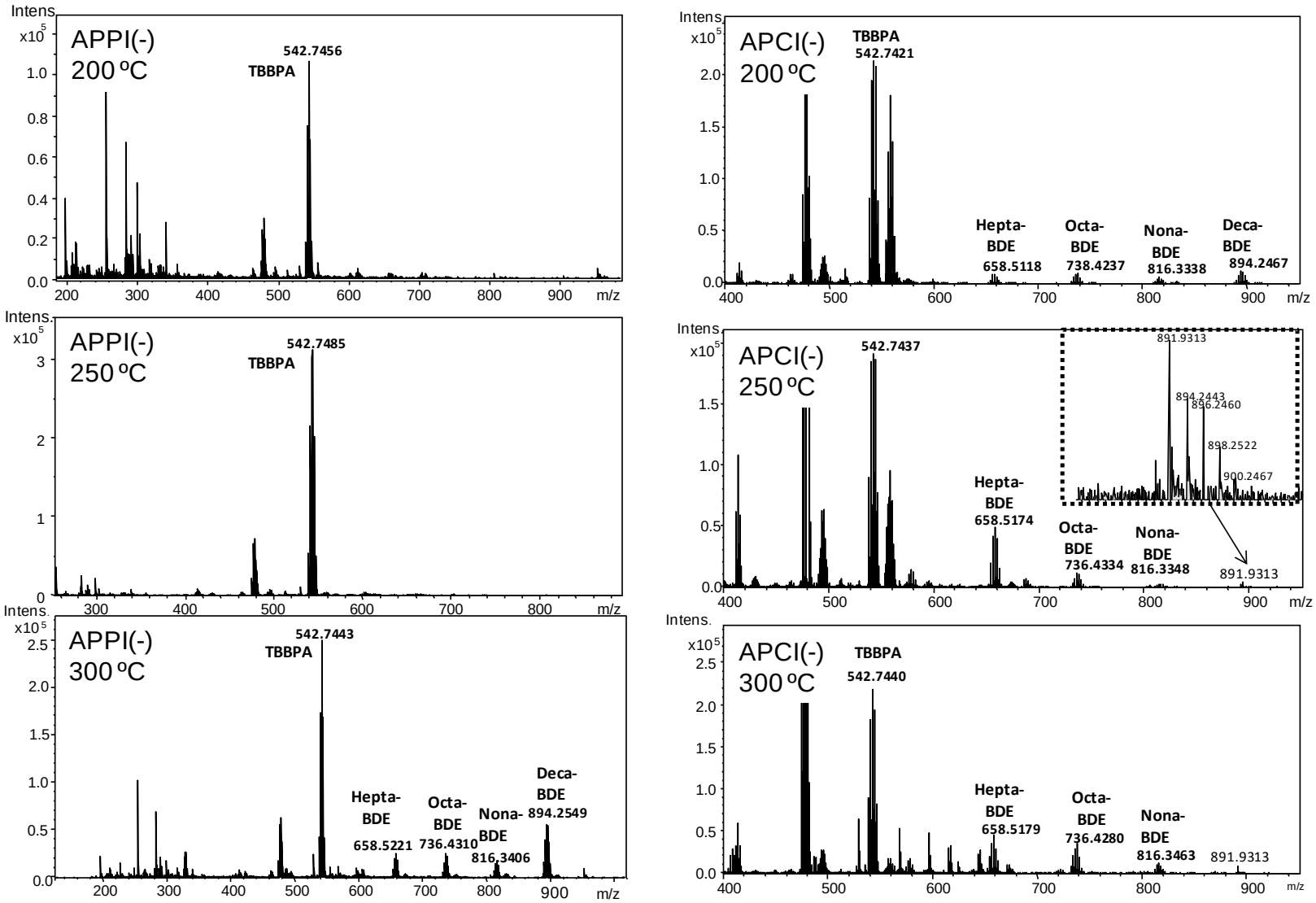

Slider
(used to move the capillary in and out of the source)
Capillary grip
Slider Track
Capillary
(surface to deposit the sample)
Pneumatic gas attachment
(nebulizer gas for desorbing compounds off capillary and vent the vaporizer tube)
Mount
(secures the DIP to the source)

Figure 2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TBBPA
APPI(-)
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TBBPA
APPI(-)
300 ºC
542.7443
TBBPA
Hepta-BDE
658.5221
Octa-BDE
736.4310
Nona-BDE
816.3406
Deca-BDE
894.2549
APCI(-)
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Nona-BDE
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894.2443
896.2460
898.2522
900.2467
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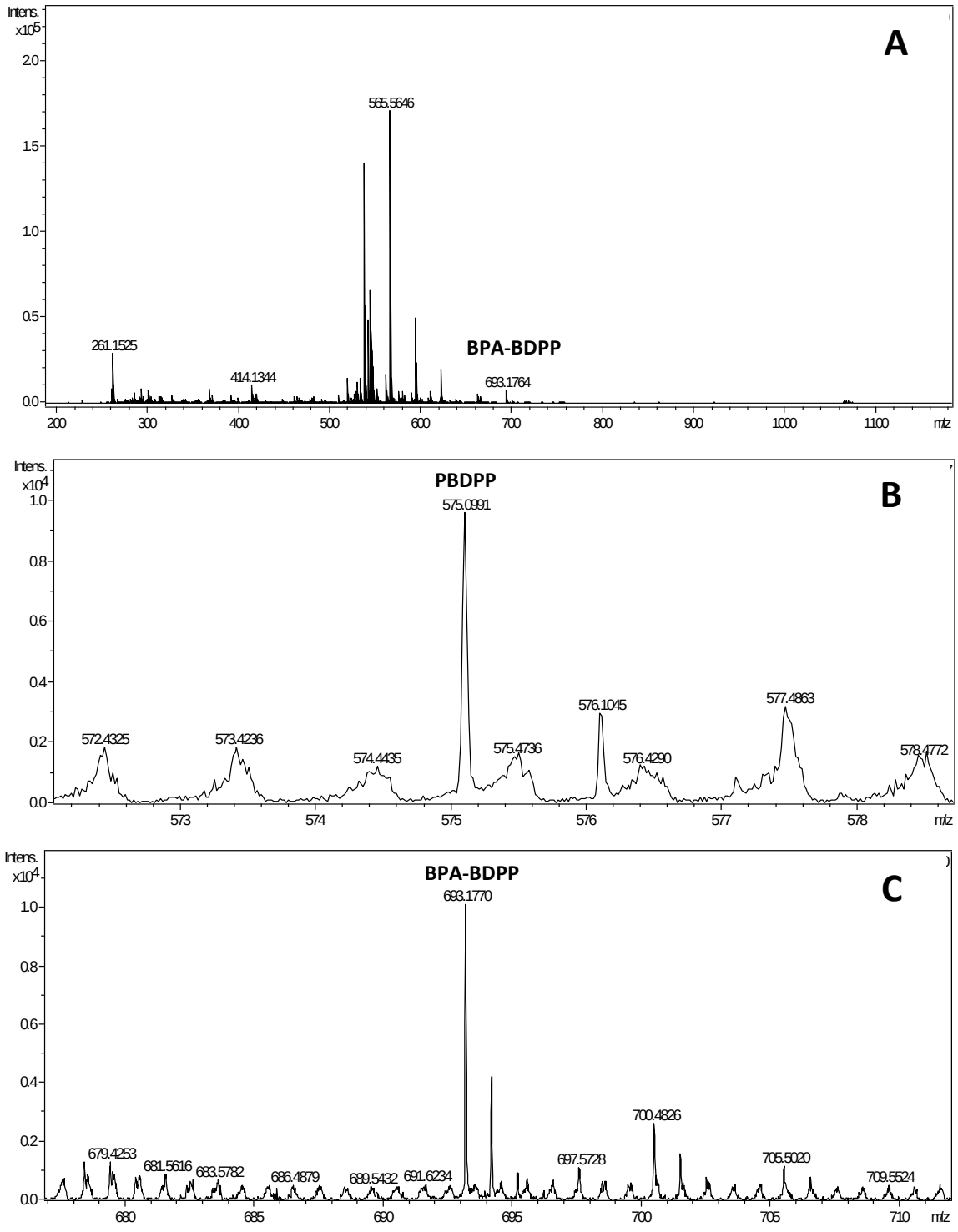
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m/z
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709.5524
m/z

Figure 3