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Fast gas chromatography-atmospheric pressure (photo)ionization mass spectrometry of polybrominated diphenylether flame retardants

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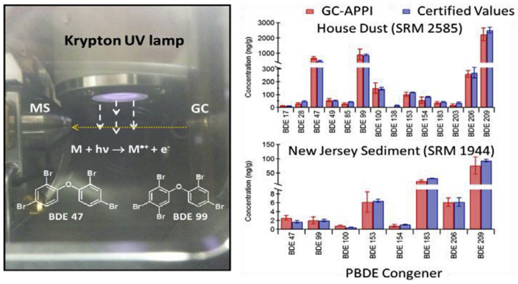
HIGHLIGHTS

- PBDEs are analyzed using commercial (GC-APCI) and custom-built (GC-APPI) ion sources.
- Separation is achieved in a fraction of the time prescribed by regulatory methods.
- Avoiding mixed-mode ionization is a practical advantage of APPI over APCI.
- Photo-oxidation enabled the differentiation of critical isomers without separation.
- The methodology is “green”, enabling the use of N_2 over non-renewable He carrier gas.

GRAPHICAL ABSTRACT



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ABSTRACT

Gas chromatography (GC) and mass spectrometry (MS) are powerful, complementary techniques for the analysis of environmental toxicants. Currently, most GC-MS instruments employ electron ionization under vacuum, but the concept of coupling GC to atmospheric pressure ionization (API) is attracting revitalized interest. API conditions are inherently compatible with a wide range of ionization techniques as well high carrier gas flows that enable fast GC separations. This study reports on the application of atmospheric pressure chemical ionization (APCI) and a custom-built photoionization (APPI) source for the GC-MS analysis of polybrominated diphenyl ethers (PBDEs), a ubiquitous class of flame retardants. Photoionization of PBDEs resulted in the abundant formation of molecular ions $M^{\bullet+}$ with very little fragmentation. Some photo-oxidation was observed, which differentiated critical BDE isomers. Formation of protonated molecules $[M+H]^+$ did not occur in GC-APPI because the ionization energy of H_2O (clusters) exceeds the energy of the ionizing photons. Avoiding mixed-mode ionization is a major advantage of APPI over APCI, which requires careful control of the source conditions. A fast GC-API-MS

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Photoionization
Fast gas chromatography

method was developed using helium and nitrogen carrier gases that provides good separation of critical isomers (BDE-49/71) and elution of BDE 209 in less than 7 min (with He) and 15 min (with N_2). It will be shown that the GC-APPI and GC-APCI methods match the sensitivity and improve upon the selectivity and throughput of established methods for the analysis of PBDEs using standard reference materials (NIST SRM 1944 and SRM 2585) and selected environmental samples.

1. Introduction

The concept of hyphenating *gas* chromatography (GC) with atmospheric pressure ionization (API) mass spectrometry was an early development whose history is succinctly described by Li et al. and Benter et al. [1,2]. The popularity of API, which increased dramatically in the 1990s, was driven by the widespread adoption of electrospray ionization (ESI) for the analysis of polar (bio)molecules, initially for *liquid* chromatography applications [3]. While the majority of GC-MS instruments today still employ electron ionization (EI) and chemical ionization (CI) under high vacuum, there is renewed interest in GC-API [1,2,4–7]. This study reports on the application of two GC-API techniques, *viz.* atmospheric pressure chemical ionization (APCI) [8,9] and atmospheric pressure photoionization (APPI) [10–12] for the analysis of brominated flame retardants, a representative and well-known class of global contaminants classified as persistent organic pollutants (POPs) [13]. The benefits afforded by GC-API for POPs analysis over classical EI/CI methods include significantly enhanced sensitivity, selectivity and speed of analysis.

Under atmospheric pressure conditions, non-reactive collisions with ambient gas molecules result in stabilization of the incipient ions. Consequently, mass spectra obtained by APCI and other *soft* ionization techniques are often dominated by (quasi)molecular ions with very little fragmentation, in contrast with *hard* EI [1,14]. Recent applications of GC-APCI have exploited the improved detection limits (<1 fg on column), especially for trace levels of POPs [5,6,15–17], including the chlorinated and brominated groups of compounds identified by the Stockholm Convention [18]. POPs share common characteristics such as persistence, strong hydrophobicity, toxicity [19–21] and since its inception the Stockholm list has expanded to include selected brominated flame retardants, including polybrominated diphenyl ethers (PBDEs). While the analysis of these compounds in most environmental matrices is challenging, the enhanced sensitivity of soft ionization GC-MS compared to EI/CI may well be crucial for studies of human and wildlife exposure that are limited by sample size [22,23].

GC-APCI is currently the most popular GC-API technique, in part because it is sensitive to a broad range of compounds. The mechanism involves generation of primary ions (usually $N_2^{\bullet+}$ and $N_4^{\bullet+}$) by corona discharge followed by charge exchange [14] with analyte molecules (M). $N_2^{\bullet+}$ is sufficiently energetic to charge exchange with most organic molecules: the IE of N_2 is 15.6 eV, whereas that of M falls between 7 and 14 eV [24]. M may react with $N_2^{\bullet+}$ to form $M^{\bullet+}$, become protonated by H_3O^+ generated in an intermediate step, or in some cases undergo more complex ion-molecule reactions [14,25]. A drawback of GC-APCI is ion suppression [1], which may result from competing reactions with matrix and background molecules in the ion source. That ionization may also occur by more than one mechanism further complicates the interpretation and analysis. Under APCI conditions, a wide range of compounds eluting from the column are ionized of which the compounds of interest may represent only a small fraction and thus the development of more selective techniques is desirable.

There is growing interest in GC-APPI (atmospheric pressure photoionization) [2,10,12], which offers improved selectivity towards aromatic compounds, including brominated flame retardants and related POPs. The technique promotes ionization by directing UV light (from a Xe, Kr, or Ar lamp) at the GC effluent exiting the column. The impinging photons (8.4–11.2 eV) impart significantly less energy than EI or APCI [26,27], which may limit or prevent ionization of matrix that would otherwise interfere with the analysis. With both APCI and APPI, negatively charged ions may also be generated by reactions with free electrons in the plasma and $O_2^{\bullet-}$ [28]. It is well known that negative mode ionization is selective towards compounds with high electron affinities, including halogenated POPs [4,14,29]. Isomer differentiation of polychlorinated dibenzo-p-dioxins by reaction with $O_2^{\bullet-}$ is an early example of this, which was recently applied to Br/Cl dioxins by Fernando et al. [25].

The speed of analysis is mostly determined by the GC oven temperature program and the carrier gas flow rate, which is usually limited by the pumping capacity in an EI/CI source. There is no such restriction with an API source. The seminal paper by Blumberg and Klee [30] recommends an optimum GC oven temperature program of ~10 °C per void time to achieve good peak capacity while keeping the run time as short as possible. Thus, a higher carrier gas flow enables a faster temperature program and a shorter analysis time. Elevated carrier gas flows can result in degraded chromatographic resolution [31], but the effect of non-optimal flow can be offset by the selectivity provided by the stationary phase. Tienstra [6] were the first to realize this strategy for pesticide residue analysis.

Herein we report on the use of two atmospheric pressure ionization techniques, *viz.* a commercially available APCI source and custom built APPI source, for the GC-MS analysis of polybrominated diphenyl ethers (PBDEs). Fast GC methods were developed using both helium and nitrogen as the carrier gas and their performance was evaluated using standard reference materials and selected environmental samples (biota, fly ash, sediment and soil). The benefits and drawbacks of the two ionization techniques are discussed with respect to their sensitivity towards the PBDEs as well as the implications for other (emerging) POPs.

2. Experimental

2.1. GC-APCI and GC-APPI experiments

The experiments were performed using a Waters Xevo G2-XS quadrupole time-of-flight (QTOF) mass spectrometer (Wilmslow, UK) coupled to an Agilent 7890B gas chromatograph [25,32]. The development and construction of the GC-APPI prototype has been described elsewhere [33]. Briefly, the photoionization lamp was mounted through the top of a modified atmospheric pressure gas chromatography (APGC) source housing (part number 289004635). The ion volume normally used during GC-APCI experiments was replaced with a standard cone gas nozzle (part number 700004216) for the APPI experiments. The lamp was positioned approximately 5 mm from the stream of GC effluent (see SI Fig. 1) and the APGC transfer line was adjusted so as to minimize the distance between

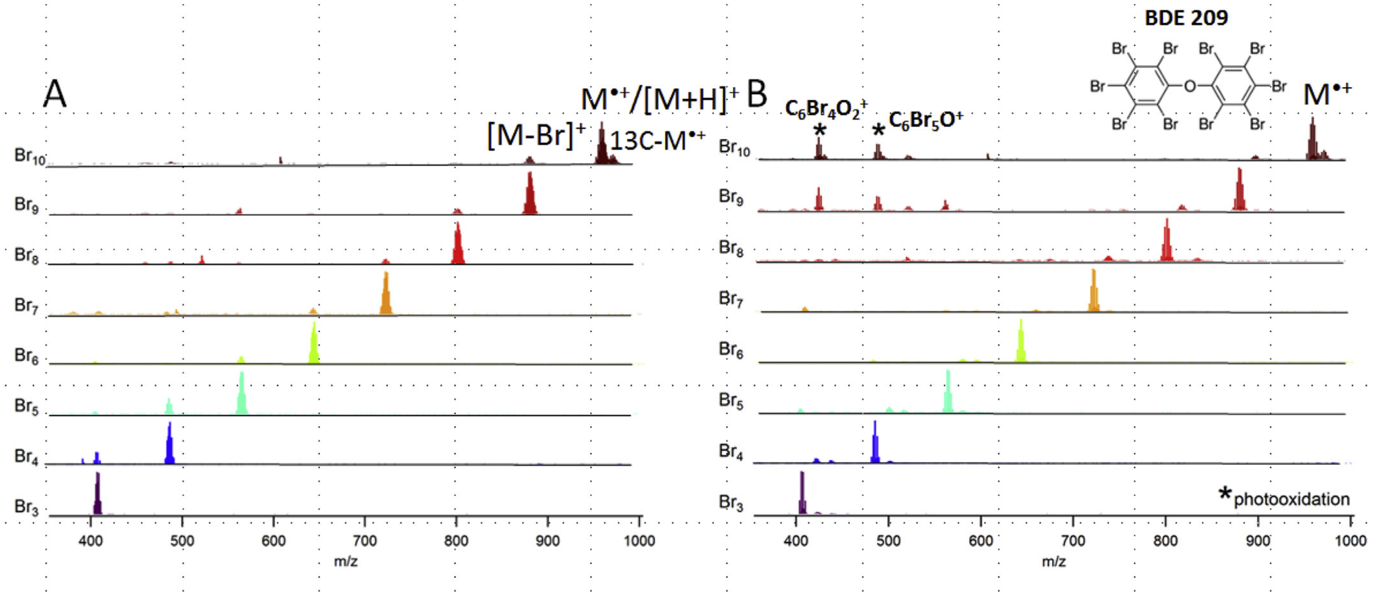

Fig. 1. (a) APCI and (b) APPI (Kr lamp) mass spectra of selected (Br_3-Br_{10}) PBDE congeners. The (*) indicates the presence of photooxidation/dissociation products in the APPI spectra that are absent in the APCI spectra.

the column end and the MS.

The ion source temperature was held at 150 °C (maximum setting) and the cone and source offset voltages were set to 20 V and 80 V. Transfer line temperatures were 340 °C and 360 °C for GC-APCI and GC-APPI experiments respectively, with a make-up flow (UHP N_2) of 350 mL/min. That the GC-APPI experiments required an elevated transfer line temperature may be the result of increased cooling of the GC column end by auxiliary and cone gas flows. The region around the column end (see SI Fig. 1) is normally enclosed in GC-APCI experiments. The optimum cone and auxiliary gas flows (N_2 from a Parker generator) for GC-APPI (175 L/h and 100 L/h) were somewhat different than the optimum flows for GC-APCI (100 L/h and 175 L/h). Even under optimized conditions, the GC eluent travelling through the ionization region experienced turbulent flows as witnessed from the chromatograms shown in SI Fig. 2. The stability of the signal may also depend on the orientation of the GC column relative to the UV lamp and MS orifice [34]. Fortunately, the instability observed at a high acquisition rate (30 scans/second) is dampened significantly when the instrument is set to acquire ~10 data points per chromatographic peak (~3 scans/second). The turbulence did not appear to negatively impact quantitation, as discussed below. A Kr lamp was used for most of the experiments reported in this study. The yield of ions generated by Ar (11.2 eV photons) and Xe (8.4 eV photons) lamps was approximately 10% of that obtained using the Kr lamp (10eV photons). This effect is the result of lower flux (in the case of the Ar-lamp) and low ionizing energy (in the case of the Xe-lamp) of the photons (Note: the photon flux is specified by the lamp manufacturer (Heraeus Holding GmbH, www.heraeus.com). Toluene and acetone vapour were introduced as dopants to the source, but generally, we observed a reduction in analyte signal in these experiments. Under these conditions $[M+H]^+$ ions are preferentially formed over $M^{\bullet+}$ radical cations. Mass spectra were collected from *m/z* 50–1000 at high resolving power (RP > 20,000 full width half maximum). Quantitative analysis of the PBDEs was performed with the instrument operating in the MS/MS mode (collision energy = 30V), by monitoring the $M^{\bullet+}$-Br_2 loss [35].

Chromatographic separation was performed using a Rtx-1614 (15 m × 0.25 mm x 0.1 μm) column. The high transfer line temperature necessitates the attachment of 0.7 m of 0.18 mm sulfinert tubing (Restek Corporation, Bellefonte, PA) to the end of the GC column. The GC inlet temperature was held at 280 °C and the oven temperature program used for analysis with He carrier gas was: 90 °C hold for 1 min; ramp at maximum heating rate to 330 °C (95 °C/min to 115 °C; 65C/min to 150 °C; 45 °C/min to 210 °C; 35 °C/min to 280 °C; 30 °C/min to 310 °C; 25 °C/min to 330 °C) and hold

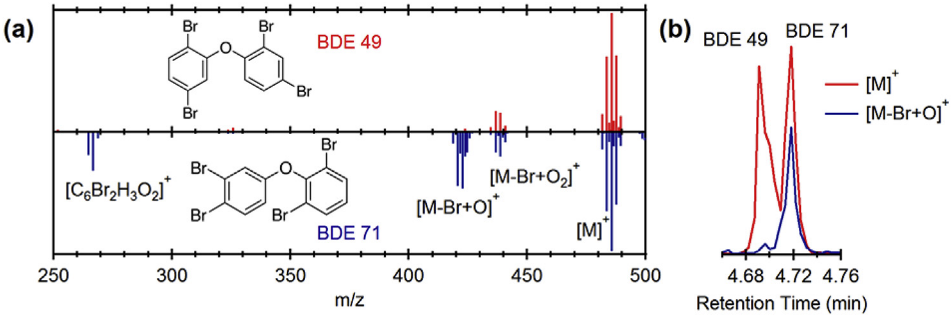

Fig. 2. (a) Isomer specific photooxidation products for BDE-Br_4 congeners BDE-49 and BDE-71. (b) Peak deconvolution of critical separation using isomer-specific photooxidation product ions.

for 5 min, with a total run time of 10 min. The oven temperature program for the analysis using N_2 carrier gas was: 90 °C hold for 1 min; ramp at 17.5 °C/min to 330 °C and hold for 5 min, with a total run time of 20 min. A constant flow (3 mL/min) of helium or nitrogen was used for the carrier gas. The injection volume was 1 µL and the samples were injected twice: once in the splitless mode and another with a 10-fold split (split time = 0.5 min).

2.2. Sample analysis by (EI) high resolution mass spectrometry

The samples in this study were also analyzed using a Micromass Premier double-focussing magnetic sector mass spectrometer of EBE geometry (Wilmslow, UK) coupled to an Agilent 7890 gas chromatograph (Santa Clara, California, USA) [36]. The GC was fitted with a 15 m × 0.25 mm x 0.1 µm DB-5ht (5% phenyl) column. The GC inlet and oven temperatures were the same as in the GC-APCI/APPI experiments, but the transfer line and EI source were held at 280 °C. The HRMS was operated at a resolving power of 10,000 (10% valley) and target compounds were detected using selected ion monitoring. Internal mass calibration was performed using lock mass ions generated from perfluorokerosene (PFK) for each voltage scan function. The injection volume was 1 µL and the injector was operated in the splitless mode.

2.3. Sample extraction and quality control

The performance of GC-APCI/APPI for the analysis of PBDEs was assessed through the analysis of standard reference materials SRM 1944 and SRM 2585 [New York/New Jersey Waterway Sediment and House Dust respectively; NIST (National Institute of Standards and Technology), Gaithersburg, MD]. Extractions of approximately 1 g of sediment (n = 1) and 50 mg samples of house dust (n = 5) were performed by pressurized liquid extraction [36] without subsequent cleanup. The samples were concentrated to 200 µL in nonane. Archived fish (n = 5), fly ash (n = 2) and soil (n = 1) samples, previously extracted and cleaned according to MECP method E3430 [36], were also analyzed. Briefly, the samples are air dried, ground, homogenized, and extracted by Soxhlet using 200 mL of Toluene. The extracts are subsequently reconstituted into 5 mL of hexane, cleaned using multi-stage silica (acid/base/$AgNO_3$) a final separation stage on alumina. The final extract is in 20 µL of nonane. Method detection limits (MDLs) were determined using blank matrix samples (Ottawa Sand) (n = 8), fortified with known quantities of native and labelled PBDE standards that yield approximately 10:1 signal-to-noise. An MDL for each congener is calculated by multiplying the standard deviation of the measurements from the fortified matrix samples (n = 8) by the t-value (98% interval) for n-1 samples.

2.4. Analytical standards and quantitation

Quantitation of the PBDEs was performed using isotope dilution mass spectrometry (IDMS): ^{13}C-lablled internal standards were added prior to extraction: $^{13}C_{12}$ BDEs 28, 47, 77, 99, 100, 126, 153, 154, 169, 183, 197, 205, 208 and 209 (Wellington Laboratories, Guelph, ON, Canada). The recoveries were verified by comparison with $^{13}C_{12}$ BDEs 79, 139, 180 and 206 (Wellington Laboratories) added prior to injection.

2.5. Density functional calculations of proton affinities

Proton affinities (in kJ/mol) were calculated with the B3LYP/6-311G (2d,d,p) level of theory using the GAUSSIAN 16 Suite of programs [37,38] on SHARCNET.

3. Results and discussion

3.1. Gas chromatography-atmospheric pressure ionization of PBDEs

The APCI and APPI mass spectra of selected Br_3-Br_9 PBDE congeners are displayed Fig. 1a and b respectively. As expected, the soft ionization techniques predominantly yield molecular ions $M^{\bullet+}$. Very little fragmentation (by Br loss) is observed in contrast to the appearance of the corresponding EI mass spectra [39]. At first glance, it is surprising that low molecular weight fragment ions are more abundant in the APPI mass spectra than in the APCI spectra, see Br_9 and Br_{10} congners (Fig. 1ab/), because the incipient molecular ions are imparted with less energy during APPI (Kr lamp, 10 eV) than in APCI (Charge exchange, 15.6 eV). This observation points to the occurrence of photooxidation, a process which has not been observed previously during LC-APPI studies of PBDEs [40]. In the experiments presented here, BDE209 for example, photodissociates into $C_6Br_5O^+$ and $C_6Br_4O_2^{+}$. Photooxidation of PBDEs is not only relevant to their analysis as these processes may also play a role in the environmental fate of PBDEs [41].

To confirm the occurrence of photooxidation, additional oxygen was introduced to the GC-APPI ion source by replacing the UHP N_2 make-up and auxiliary gases with N_2 purified from a generator, which contains approximately 1% oxygen. The result of this experiment (see Figure SI3) indicates that the yield of photooxidation products increases two-fold when additional oxygen is introduced. The observation of such reactions is serendipitous as it appears they have structure diagnostic value, unlike the dissociations observed under EI and APCI conditions: the EI/APCI mass spectra of isomeric BDEs are virtually identical [39], whereas, the APPI mass spectra obtained for the tetrabromo isomers BDEs 49 and 71, see Fig. 2a, are quite different. BDE 71 undergoes photooxidation/dissociation resulting in Br/O and Br/O_2 exchange products as well as $C_6Br_2H_3O_2^{+}$, whereas photooxidation of BDE 49 only produces $[M\text{-}Br + O_2]^+$.

This observation is significant because BDEs 49 and 71 are a critical pair according to EPA method 1614 [42], which prescribes <30% baseline separation of the two isomers. As shown in Fig. 2b, GC separation of the pair (red trace) is possible, but the intense photooxidation product $[M\text{-}Br + O]^+$ may be used to specifically select BDE 71. Reactions involving O_2 in the negative ion mode have been shown to be of similar structure diagnostic value for differentiating mixed halogenated POPs [25,28]. Examples of reactions between positive ions and O_2 are rarer [43]. Apart from the implications to structure analysis, the reactions observed here (likely due to the presence of oxygen and/or water) may be important in photolytic degradation of PBDEs in the environment. Pan et al. [40] have noted that few experimental studies have been performed on the photolysis of PBDEs in the gas-phase and GC-APPI may well be a useful platform to study these processes [44].

One drawback associated with using APCI for PBDE analysis is the potential for reactions with H_3O^+, generated from residual water in the ion source. This is apparent from Fig. 3a (bottom), which displays the partial APCI mass spectrum of BDE 209 (and its 13C-labelled counterpart): both $M^{\bullet+}$ and $[M+H]^+$ ions are present. This is undesirable because: (i) the formation of two (quasi)molecular ions splits the signal intensity resulting in higher detection limits; and (ii) it also obfuscates the isotope pattern and complicates interpretation.

The relative abundance of ions $[M+H]^+$ can be influenced by the source gas settings, but nevertheless the yield is still be difficult to control: water originating from laboratory humidity will adsorb to the metal surfaces of the ion source when the housing is opened, leading to long-lasting effects to the appearance of the mass spectrum. Instead of trying to exclude the presence of H_2O, it can be

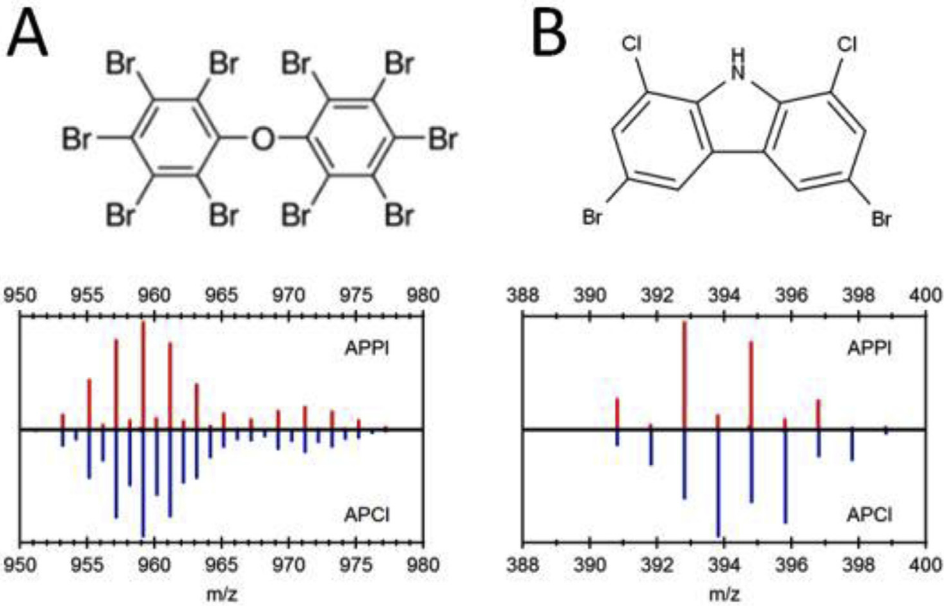

Fig. 3. Partial mass spectra obtained using APPI (top) and APCI (bottom) for (a) decabromo-diphenylether (BDE209) and its 13C-labelled counterpart, and (b) 1,8-dibromo-2,6-dichloro-9H-carbazole. APPI generates $M^{\bullet+}$ ions only, whereas APCI results in a mixture of $M^{\bullet+}$ and $[M+H]^+$ ions.

deliberately introduced (by placing a vial in the source housing) to drive the formation of $[M+H]^+$ [45]. However, such conditions are unsuitable for the analysis of PBDEs and related compounds (e.g. most POPs) that have relatively low proton affinities (PAs). The PA of BDE 209 has not been measured, but our density functional calculations indicate that protonation may either occur at the oxygen (773 kJ/mol) or on the ring (792 kJ/mol). These values are only marginally higher than that of H_2O (691 kJ/mol) [24] and lower than that of H_2O cluster ions [46]. Thus, poor ionization efficiency and competition with other compounds with higher PAs likely explains why the yield of PBDE ions (and dioxin ions [5]) is low when H_2O is introduced to the ion source.

The APPI spectrum (Fig. 3a, top) does not suffer from the same problem of mixed-mode ionization: it displays only $M^{\bullet+}$ ions because the impinging photons are not sufficiently energetic to ionize water. The contrast between APCI and APPI is even more dramatic for 1,8-dibromo-2,6-dichloro-9H-carbazole, see Fig. 3b (top vs. bottom), which belongs to an emerging class of POPs believed to occur as by-products of halogenated indigo dyes [47,48]. $[M+H]^+$ ions dominate the APCI spectrum because the presence of nitrogen increases its PA_N (844 kJ/mol), although protonation likely also occurs on the ring ($PA_{ring} = 845$ kJ/mol) [49]. Despite the higher PA, the APPI experiment results in the formation of only one population of molecular ions, *i.e.* $M^{\bullet+}$.

These results may serve to show the significant advantage of APPI over APCI. The influence of *protomers* on the analysis may be further investigated using ion-mobility [49,50].

3.2. Fast gas chromatographic separation using helium and nitrogen carrier gases

Fig. 4a (top) displays the extracted ion chromatogram of the tetrabromo BDEs obtained by GC-APCI, with the Helium carrier gas flow set for optimum efficiency (1.4 mL/min). At this flow setting, the optimum heating rate [30], estimated from the void time, is 17.5 °C/min. The bottom panel of Fig. 4a was obtained under the same conditions except N_2 was used as the carrier gas. Nitrogen is a slower carrier gas than helium to provide similar separation efficiency [30] and thus it is not surprising that the peak widths in the N_2 carrier gas experiment (Fig. 4a, bottom) are approximately double those observed in the He carrier gas experiment (Fig. 4a, top). We also note that the critical pair BDE 49/71 is baseline resolved with He, whereas there is a ~10% valley when N_2 is used. Nevertheless, the separation is satisfactory and meets the criterion (40% valley) prescribed by EPA method 1614 [42]. It is gratifying to note that the highest congener, BDE 209, elutes in <15 min, which is significantly faster than the 52 min (!) run time reported in the EPA method.

As the carrier gas flows and optimum heating rates are increased, see Fig. 4 b/c, the analysis time decreases. The criterion to separate BDEs 49/71 is still achievable with a N_2 carrier gas flow (2.8 mL/min) well above the optimum flow (0.5 mL/min) and the total analysis time is reduced to <10 min! This observation underlines the importance of stationary phase selectivity to compensate for diffusion during the course of a chromatographic separation. At 5.6 mL/min N_2, the BDE 49/71 peaks coalesce, but as noted in the section above, reactions with oxygen/water (under APPI conditions) can be used to distinguish the two isomers when co-elution occurs. While N_2 cannot yield better performance than He or H_2 carrier gases, it may convenient to use because it is relatively inexpensive and it is not associated with the same safety concerns of H_2 or the finite supply of He that is prone to disruption.

A laboratory rich in helium may significantly improve their throughput as shown in Fig. 3c (top) and 3d, because good quality separations can be obtained in under 7 min using He. The 40% valley is not yet reached in Fig. 3c and, in principle, analysis times closer to 3–4 min could potentially be realized. However, the experiments described here were performed using a conventional GC oven, which imposes a practical limit to the oven heating rate.

The experiments reported in Fig. 4 were performed using APCI, but as shown in Fig. 5, similar relative responses are obtained using APPI. For the evaluation and validation experiments presented in the next section, we have chosen a He flow rate of 3 mL/min and the maximum ramp rate provided by a conventional GC oven (see experimental).

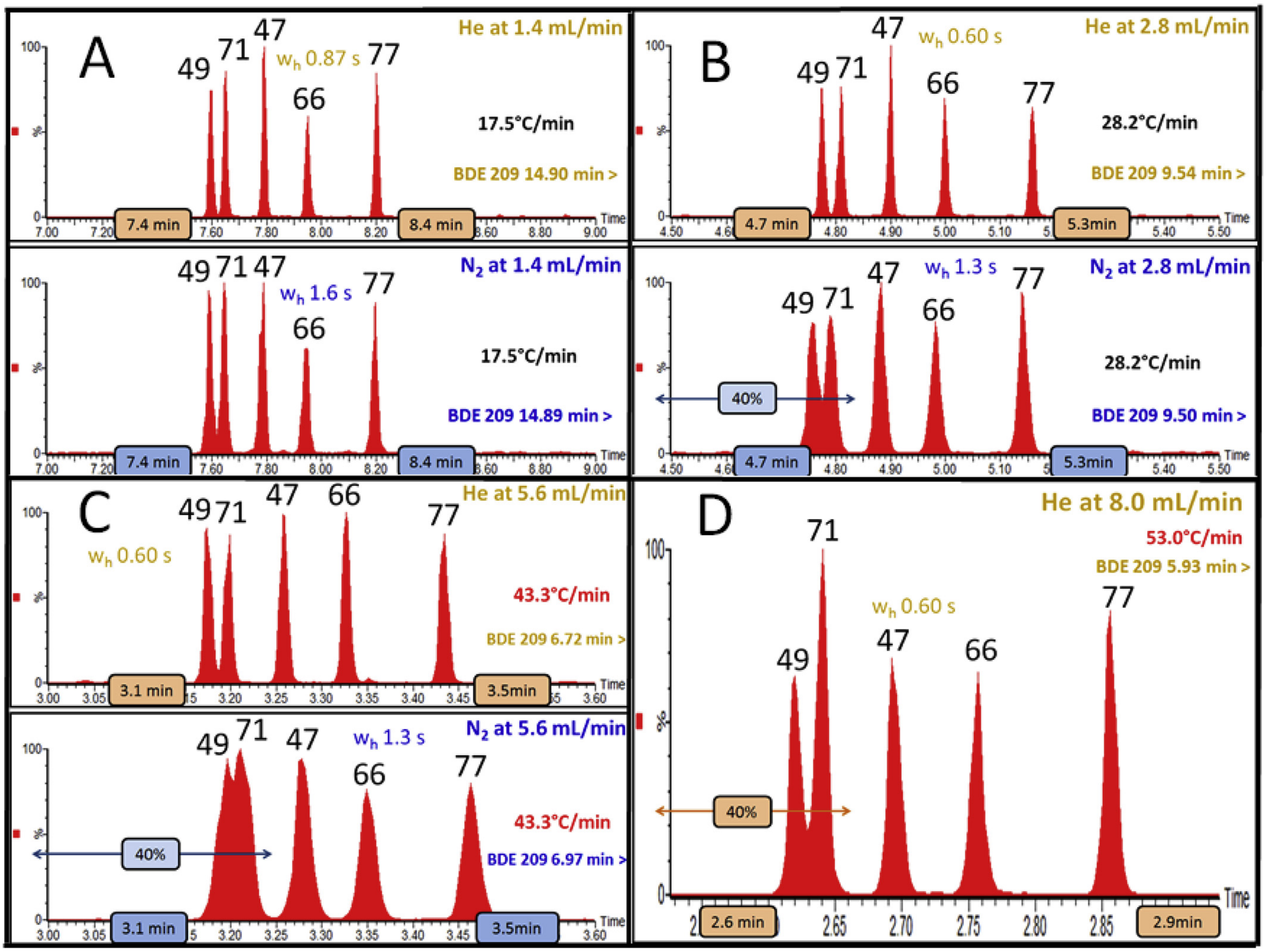

Fig. 4. Extracted ion chromatograms of tetra-BDEs using: (a) 1.4 mL/min of He (top) and N_2 (bottom); (b) 2.8 mL/min of He (top) and N_2 (bottom); (c) 5.6 mL/min of He (top) and N_2 (bottom); (d) 8.0 mL/min of He.

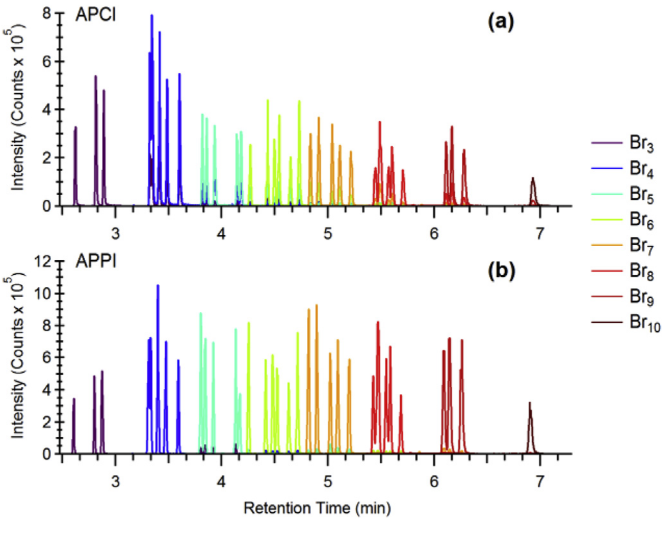

Fig. 5. Extracted ion chromatograms of (Br_3-Br_{10}) -BDEs obtained by: (a) GC-APCI; and (b) GC-APPI.

3.3. Evaluation and validation with reference materials and environmental samples

In this section, the performance of two methodologies are evaluated using reference materials and results obtained by a regulatory method (MECP method E3430 [35]) using a magnetic sector instrument (GC-HRMS). The GC-APCI analyses were performed with N_2 as the carrier gas (<15 min run time) and the GC-APPI analyses were performed using He (<7 min run time). Both APCI and APPI methodologies performed very well for the analysis of the two certified reference materials SRM 2585 and SRM 1944, which are household dust and New York/New Jersey waterway sediment samples respectively. All measured values are within 30% of the certified values, see Fig. S4 and Table S1. Within-run and between-run repeatability were between 4 − 47% and 7–45%.

A set of environmental samples, including fish, sediment and fly ash, that had previously been analyzed using a magnetic sector instrument were also injected into the GC-APCI instrument. A summary of the results is given in Fig. 6a, which displays good correlations between the PBDE concentrations measured using the two techniques and the standard HRMS method over approximately five orders of magnitude. (Note that the samples were injected twice: once in the splitless mode and another with a 10-

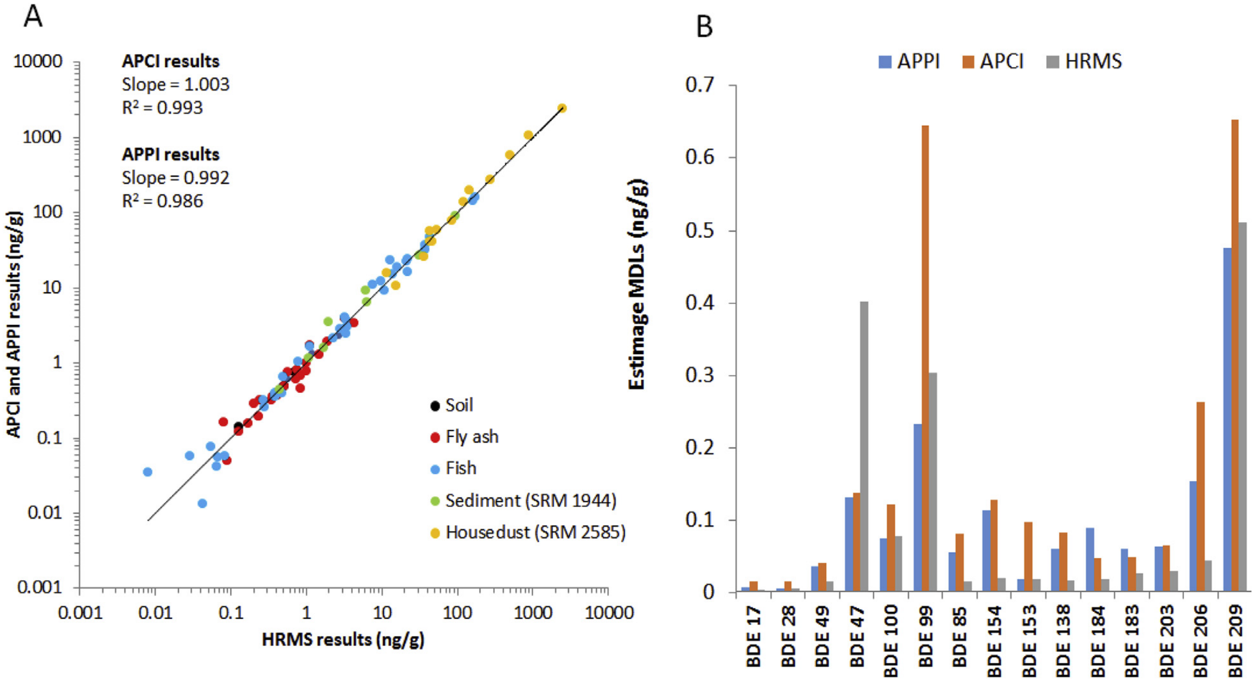

Fig. 6. (a) Comparison of PBDE concentrations in environmental samples obtained using GC-APCI and GC-HRMS; (b) Comparison of method detection limits for soil/sediment analysis of PBDEs obtained using GC-APPI, GC-APCI and GC-HRMS (MECP Method E3430 [35]).

fold split. The dynamic range of the QTof instrument is limited to ~4 orders of magnitude). The performance of the APCI and APPI methodologies are quite close: the slopes correlating the APCI and APPI results to the HRMS results are 1.003 and 0.992 respectively. The relative differences $[(X_{APCI/APPI}-X_{HRMS})/X_{HRMS}]$ between the APCI/APPI and the HRMS results of individual congeners was <30% for >80% of the measurements. The remaining (c. 20%) APCI/APPI measurements approach the detection limits of the three techniques, but are still within a factor of two of the HRMS results.

Fig. 6b compares the method detection limits (MDLs) obtained using GC-APPI, GC-APCI and GC-HRMS. We ascribe the slightly better performance of HRMS to the method of detection rather than ionization. The APPI and APCI results were obtained using a time-of-flight analyzer, which may provide more variable results compared to magnetic sector and tandem quadrupole mass spectrometers [51]. Apart from two congeners, the APPI MDLs are lower than those obtained by APCI. This result may reflect the fact that APCI conditions are more difficult to optimize due to the presence of water and the generation of mixed populations of (quasi)molecular ions in the source, compared to APPI. Overall, the APPI and APCI derived MDLs are satisfactory and compare well with the HRMS MDLs.

4. Conclusions

The hyphenation of gas chromatography with atmospheric pressure ionization (API) offers significant advantages in sensitivity, selectivity and speed of analysis, over traditional (EI) GC-MS methodologies. In undergraduate laboratories, students are often taught the “rule of thumb” that the number of minutes of GC analysis time is approximately equal to the number of meters of capillary column. Herein, we demonstrate that PBDEs are efficiently separated in only a fraction of the time (c. <7 min with He carrier gas; <15 min N_2) prescribed by regulatory methods (e.g. 52 min - EPA Method 1614 and > 20 min - MECP method E3430) because of the inherent compatibility of atmospheric pressure ionization with elevated flows. Nitrogen is usually avoided as a carrier gas for GC-MS because of the negative impact on sensitivity, but such an effect is not observed under API conditions. Indeed, in the case of APCI, N_2 is the reagent. APPI is a particularly attractive technique for the analysis of aromatic POPs because of its selectivity towards low IE compounds and its use circumvents undesirable reactions with H_2O, which is a practical issue that has plagued GC-APCI studies of POPs. We have shown that soft ionization results in enhanced sensitivity: the results reported here were obtained using a QTOF instrument capable of full-scan acquisition, but are nevertheless comparable to those obtained by traditional *targeted* methodologies, *viz*. selected ion monitoring HRMS. This raises the exciting possibility that the integration of a fast GC-API-QTOF platform into research and regulatory laboratories will enable *non-targeted* identification of unknown and emerging environmental contaminants in parallel with high-throughput routine testing and monitoring.

Declaration of interests

- The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
- The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2019.01.007.

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