Determination of halogenated flame retardants using gas chromatography with atmospheric pressure chemical ionization (APCI) and a high resolution quadrupole time of flight mass spectrometer (HRqTOFMS).

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ABSTRACT: A method to analyze halogenated flame retardants was developed that utilizes gas chromatography with atmospheric chemical ionization (APCI) high resolution quadrupole time of flight mass spectrometry (HRqTOFMS). The new GC-APCI-HRqTOFMS method was used to determine the presence of 65 halogenated flame retardants (HFRs) in the United Sates National Institute of Standards and Technology (NIST) organic contaminants in house dust standard reference material (SRM). The accuracy of the measurements were compared to the certified NIST value for polybrominated diphenyl ethers (PBDEs) and had an average accuracy for the 14 certified PBDEs of 109 % with sub picogram detection limits (on column) from a single 1 µL injection with a run time of 18 minutes. SRM2585 extracts were also analyzed by GC electron ionization (EI) high resolution mass spectrometry (HRMS) and there was an excellent correlation between the two datasets (R^2 value of 0.996). The presence of twenty five additional HFRs were also screened in the dust standard and ten were detected in concentrations above the limits of detection, these were p-TBX, PBBZ, PBT, PBEB, TDCPP, HBBZ, EHTBB, TBBPA, BEHTBP and BTBPE. The results presented show that the proposed APCI-HRqTOFMS method was comparable and in many cases an improvement on the existing EI-HRMS method.

Flame retardants have been used for thousands of years[1], however the development of halogenated flame retardants (HFRs) has only occurred during the last century or so. Analytical and toxicological developments continue to identify the use of many of these organic flame retardants as a potential environmental concern.[2] The production and use of many halogenated flame retardants including; the penta and octa BDE formulations, pentabromobenzene (PBBZ) hexabromobiphenyl, and hexabromocyclododecane (HBCDD) have been phased out due to EU legislative measures and designated as persistent organic pollutants.[3] However, many of the replacements for these banned substances are often very chemically similar and therefore not surprisingly are beginning to be identified in the environment .[4-10]

The analysis of halogenated flame retardants is not straightforward. Some flame retardants such as hexachlorocyclopentenyldibromocyclooctane (HCDBCO) and 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) can be determined relatively easily using existing techniques for PBDEs.[10] However, there is a large range in physiochemical properties of HFRs and so analysis of all HFRs in one method can present several difficulties. As a consequence of this HFRs have been determined using various different techniques, including both gas chromatography (GC) and liquid chromatography (LC). A detailed list of analytical techniques that have been used for the analysis of HFRs is documented by Covaci et al.[10] One thing that many of these methods all share is that they are targeted methods designed to determine a specific set of HFRs. Existing GC methods include electron capture negative ion mass spectrometry (ECNI-MS)[11], tandem mass spectrometry (MS/MS)[12] and high resolution mass spectrometry (HRMS).[13]

Over the past decade or two the magnetic sector instrument (HRMS) has been considered by many to be the 'gold standard' for targeted compound analysis in environmental reaserch.[14] Modern double focusing magnetic sector instruments tuned to achieve a resolution of >10,000, can achieve sub-femtogram levels of detection, and have an excellent dynamic range of 6 to 7 orders of magnitude.[14] Analysis is undertaken using selective ion monitoring (SIM) where several target ions are selectively passed onto the detector. Whilst this decreases the detection limits by a factor of 10 to 100 it means that only a limited number of compounds can be determined at any one time.[14] This is not a significant issue when analyzing for a group of compounds such as PCBs or PBDEs that have highly ordered elution times, however when analyzing emerging halogenated flame retardants this can be problematic as there are many dif-

ferent ions to monitor. To determine a wide range of HFRs, several analytical runs can be required to cover the full range of possible compounds. Using SIM analysis also has the limitation of not collecting data for anything but the target ions. It is therefore less well suited as a wider screening tool to search for new contaminants or breakdown products in environmental samples.

A new approach to determine halogenated flame retardants is proposed that offers not only an improved sensitivity and selectivity to the traditional EI-HRMS methods but the ability to collect full scan data so that samples may be screened for other contaminants of concern. This approach utilizes atmospheric pressure chemical ionization (APCI) and detection using a high resolution quadrupole time of flight mass spectrometer (HRqTOFMS). Atmospheric pressure chemical ionization is an ionization technique that has been around since the 1970s. [15,16] However, these early applications used a ^{63}Ni foil to induce ionization whereas the current instrumentation utilizes a plasma discharge from a corona pin to induce ionization. Historically, APCI has been largely overlooked for the analysis of HFRs, however Debrauwer et al. [17], Cariou et al. [18] and Zhou et al. [12] showed that HFRs could be effectively ionized by APCI. The advantage of using an APCI source is that the soft ionization normally results in limited fragmentation which can boost sensitivity as the resultant mass spectra are generally dominated by the molecular or quasi molecular ion. The method proposed here utilizes gas chromatography, ionization by APCI and detection by HRqTOFMS. It is capable of performing both targeted and non-targeted analysis of halogenated flame retardants with sub picogram detection limits (on column) from a single injection with a run time of 18 minutes. The method was tested to screen for the presence of 65 HFRs (40 BDEs and 25 additional flame retardants) in the United States National Institute of Standards and Technology (NIST) standard reference material SRM 2585 – organic contaminants in house dust.

Experimental Section

^{13}C Labeled Internal Standards. Quantitation of the HFRs was undertaken using a combination of $^{13}C_{12}$ isotopically labeled internal (surrogate) standards added at the point of extraction and $^{13}C_{12}$ isotopically labeled injection (syringe) standards added just prior to analysis. The internal standard mixture consisted of the following labeled compounds, $^{13}C_{12}$ BDEs 3, 15, 28, 47, 77, 99, 100, 126, 153, 154, 169, 183, 197, 205, 207 and 209 (Wellington Laboratories) and the $^{13}C_{12}$ labeled HFRs Dechlorane plus *syn* (Cambridge Isotope Laboratories), EHTBB (Wellington Laboratories), BEHTBP (Wellington Laboratories), HBBZ (Wellington Laboratories), HBB-153, BTBPE (Wellington Laboratories) and DBDPE (Wellington Laboratories). The injection standard contained the $^{13}C_{12}$ labeled BDEs 79, 139,180 and 206 (Wellington Laboratories) and Dechlorane plus *anti* (Cambridge Isotope Laboratories). Where available the analyte in question was quantified off the appropriate internal standard and if not then the appropriate injection standard. Full names and mass spectra of all HFRs determined are presented in the supporting information as SI 1.

Sample Extraction. Approximately 0.1 g of dust was accurately weighed into a clean 20 ml glass vial. This was spiked with 10 µL of labeled internal standard and 10 ml of HPLC grade DCM (Caledon Laboratories) added. The sample was then sonnicated for 15 minutes. The solvent was decanted and the extraction repeated twice more. The combined extracts were then evaporated to approximately 1 ml using an automated N_2 evaporator (Labconco, USA), transferred to a 2 ml amber glass GC vial, blown down to 1 ml using a stream of high purity N_2 (Grade 5.0, Linde, Canada) and the injection standard added. No sample clean-up was undertaken.

Sample Analysis by APCI-HRqTOFMS. Samples were analyzed using a Waters Xevo G2-XS qTOF fitted with a 15 m x 0.25 mm x 0.1 µm DB-5 HT (5% phenyl) GC column. This was connected to a 0.8 m x 1.8 mm sulfinert treated MXT tubing in the transfer line, following guidance from Organtini et al.[19] The injector temperature was set at 280 ^{0}C, and transfer line at 330^{0}C. The initial oven temperature was set at 110 ^{0}C with a ramp of 40^{0}C a minute to 200 ^{0}C, 10 ^{0}C a minute to 280 ^{0}C and 30 ^{0}C a minute to 330 ^{0}C and held for 5 minutes, resulting in a total run time of 17.92 minutes. The corona voltage was set at 5 mAu, the cone gas at a flow rate of 175 L hr^{-1} and the desolvation gas flow set at 175 L hr^{-1}. Ionization was undertaken using an atmospheric pressure chemical ionization source at 150 ^{0}C with the detector run in full scan mode using the seven target enhanced functions presented in Table 1. The target enhanced function works by adjusting the timing of the pusher at the exit of the quadrupole region to optimize the transfer of the ions of the selected m/z to the TOFMS flight tube. This leads to an approximately ten fold increase in sensitivity for ions of the selected m/z. The mass spectrometer was operated at a resolving power of >20,000 full width at half maximum (fwhm). Internal mass calibration was performed by using a lock mass ion (212.075) generated as background in the source region.

Table 1. Summary monitored ions and LODs for HFRs for APCI-HRqTOFMS and EI-HRMS

Substance	APCI-HRqTOF		EI-HRMS	
	Quant ion	LOD (pg µL^{-1})	Quant ion	LOD (pg µL^{-1})
Mono-BDEs	247.984	***0.12***	247.984	0.38
Di-BDEs	327.892	***0.013***	327.892	0.014
Tri-BDEs	405.803	0.060	405.803	***0.036***
Tetra-BDEs	485.711	0.13	485.711	***0.062***
Penta-BDEs	563.622	***0.042***	563.622	0.075
Hexa-BDEs	643.530	***0.032***	485.693	0.20
Hepta-BDEs	721.441	***0.083***	561.606	0.49
Octa-BDEs	801.349	***0.25***	639.516	0.63
Nona-BDEs	879.259	***0.33***	719.425	1.4
Deca-BDE	959.168	***2.5***	797.335	11
ATE (*TBP-AE*)	291.894	0.15	329.771	***0.11***
α&βTBECH *(α&βDBE-DBCH)*	266.921	3.3	266.921	***0.31***
BATE	329.774	0.13	329.774	***0.05***
pTBX (*TBX*)	421.716	***0.020***	421.716	0.17
α&βTBCO	346.843	0.84	264.923	***0.35***
PBBZ	471.595	***0.020***	471.595	0.12
TBCT	441.661	0.033	441.661	***0.028***

Substance	APCI-HRqTOF		EI-HRMS	
	Quant ion	LOD (pg μL^{-1})	Quant ion	LOD (pg μL^{-1})
PBT	485.611	***0.016***	485.611	0.035
PBEB	499.627	0.46	499.627	***0.16***
TDCPP	320.920	0.28		
TBEP (*TBOEP*)	397.237	0.016		
DPTE (*TBP-DBPE*)	329.771	0.15	329.771	***0.047***
HBBZ (*HBB*)	551.504	***0.08***	551.504	0.10
PBBA (*PBB-Acr*)	476.698	***0.069***	476.698	0.29
EHTBB (*EH-TBB*)	437.675	0.31	418.674	***0.24***
HCDBCO (*DBHCTD*)	539.739	***0.30***	265.931	1.90
TBBPA	528.730	0.15		
BEHTBP (*BEH-TEBP*)	464.662	***0.11***	464.662	0.29
BB153	627.535	***0.020***	465.703	0.066
T23BPIC (*TDBPP*)	651.711	0.11		
BTBPE	687.556	***0.10***	356.795	0.56
s-DP (*s-DDC-CO*)	653.711	0.16	271.810	***0.091***
a-DP (a-*DDC-CO*)	653.711	0.15	271.810	***0.083***
OBIND (*OBTMPI*)	867.433	***0.20***	850.411	4.0
DBDPE	971.204	***9.1***	484.603	40

Sample Analysis by EI-HRMS. Samples were analyzed using a Micromass Premier HRMS fitted with a 15 m x 0.25 mm x 0.1 µm DB-5 HT (5% phenyl) GC column. The injector and oven temperatures were the same as the HRqTOFMS but the transfer line was set at a temperature of 280 ^{0}C. Ionization was undertaken using an electron ionization source at 280 ^{0}C operated in selected ion monitoring mode using the ions presented in Table 2. To maintain high levels of sensitivity and reduce the number of ions monitored the analysis was conducted using 5 different runs. The mass spectrometer was operated at a resolving power of >10,000 (10% valley), with internal mass calibration performed by using lock mass ions generated from perfluorokerosene (PFK) as specified by Kolic et al.[13] for each voltage scan function.

Results and Discussion

Instrument limits of detection. To represent a broad screen of existing and potential HFRs in the environment, solutions of 40 PBDEs and 25 emerging HFRs were mixed into six calibration solutions ranging from ~ 0.5 pg/µL (CS1) to ~ 400 pg/µL (CS5).The lowest calibration solution (CS1) was further diluted by a factor of 2 and 10 to test the instrument limits of detection (LOD). Table 1 presents the limits of detection and ions used for quantification. All standards were analyzed in triplicate and LODs calculated by serial dilution and reported with a signal to noise ratio of 10. The results presented show that the detection limits obtained using APCI-HRqTOFMS were comparable to those attained by EI-HRMS and in many cases were an improvement. Limits of detection for 15 of the 25 emerging HFRs were lower using EI- HRMS than APCI-HRqTOFMS, however the average LOD for the 25 emerging HFRs was 2.35 (0.028-40) pg μL^{-1} using EI- HRMS compared to 0.65 (0.016-9.1) pg μL^{-1} with APCI-HRqTOFMS. Limits of detection for 31 of the 40 PBDEs were lower with APCI-HRqTOFMS than EI-HRMS. The average LOD with APCI-HRqTOFMS of 0.17 (0.0123-2.5) pg μL^{-1} was again lower than the average LOD of 0.59 (0.014-11) pg μL^{-1} achieved by EI- HRMS. Detection limits, quantification and confirmation ions plus retention times for all HFRs are presented in the supporting information (SI 2) and are summarized in Table 1 where the lower of the two (APCI-HRqTOF vs EI-HRMS) detection limits is highlighted in bold and italics. The average limit of detection is listed for each level of bromination of the BDE congeners. For reference the acronyms of the emerging HFRs as suggested by Bergman et al. [20] have been included (where available) here in italics. The full names and structures of all of the selected analytes are included in SI 1.

Table 2. Target enhancement functions

	Time (mins)	Target enhanced mass (Da)	Mass window (Da)
Function 1	1 – 18	Full scan mode	100 – 1200
Function 2	2 – 5.5	290	90 – 490
Function 3	3.5 – 8	410	200 – 610
Function 4	5.5 – 14	520	200 – 720
Function 5	8.5 – 14.5	675	200 – 875
Function 6	11.5 – 16.5	840	200 – 1040
Function 7	14.5 – 18	965	200 – 1165
Function 8	Lock mass channel 212.0750		

Chromatographic separation. The chromatography was optimized in an attempt to provide baseline separation of all target compounds within a 20 minute run time. Several oven temperature ramps were trialed and adequate separation was achieved in a run time of 18 minutes using the conditions specified in the methods section. In these trials, improved separation of BDE-204/197, TBECH and TBCO was achieved but at the detriment to other analytes. Using the conditions mentioned here separation is still possible but is highly dependent on the cleanliness of the injector, therefore for routine screening of environmental samples it is preferable to report them as combined totals. For a targeted assessment of these specific HFRs gas chromatography methods outlined by Arsenault et al.[21] and Riddell et al.[22] may be considered, along with analysis by liquid chromatography[23] which should obviate the issues with temperature induced isomerization. The transfer line temperature proved a critical parameter for the separation of the octa and nona BDEs, at temperatures below 330°C these isomers began to co-elute due to peak broadening. To counteract this, the original carrier gas flow ramp was adjusted to include an increase

in flow from 1.5 ml to 4 mL min just prior to the elution of the octa BDEs. This has the added benefit of compressing and increasing the height of the octa to deca peaks and thus also lowering the detection limits for these congeners. The ability to increase the carrier gas flow to these levels without impacting the system is one of the added benefits of the APCI source i.e. the ability of the source to handle higher flow rates than would be possible for a classical vacuum based MS such as a sector HRMS. The selected ion chromatograms for all target analytes are presented as supporting information 3 (SI 3).

Linear Range. A major disadvantage of most TOF instruments is the low dynamic range. This is usually limited to 4 orders of magnitude.[14] To investigate the linear range of the instrument, a range of calibration solutions BFR-CVS (CS1 – CS5) were analyzed in triplicate. To extend the sample range CS1 was further diluted by a factor of two (CS0.5) and ten (CS0.1) and CS2, CS3, CS4 and CS5 diluted by a factor of two to produce CS1.5, CS2.5, CS3.5 and CS4.5 respectively. When using the target enhancement functions (Table 1) linearity was observed for the majority of HFRs from CS0.1 to CS5 (representing 0.025 to 100 pg uL-1 for BDE 15), although for some of the higher molecular weight compounds (>700 Da) linearity did not extend beyond CS4.5. Removing CS5 from the calibration curves gave a more accurate result but did reduce the calibration range. As the samples were simultaneously analyzed without the target enhancement a second calibration curve could be produced using the non-target enhanced data from CS1 to CS5. By combing these two approaches the linier range of compounds in lower concentrations could be quantified using the target enhanced data and compounds in higher concentrations quantified by the non-target enhanced data. These results indicate that with additional processing, analysis by APCI-HRqTOFMS is capable of matching and exceeding the linear range of a classical sector HRMS.

Ionization by APCI. An advantage of using APCI is that the soft ionization at atmospheric pressure results in very limited fragmentation which produces mass spectra that is predominantly dominated by the M+• ion which can boost sensitivity and lower detection limits. Whilst the PBDEs produced a mass spectra dominated by the M+• ion, this was not the case for all HFRs. The major fragments produced by APCI and EI were similar for the lower molecular weight HFRs, however there was far less fragmentation observed during APCI for the higher mass HFRs such as DBDPE. For quantification by APCI there were instances where the most abundant ion was not selected for quantification (e.g. TDCPP). This was done to give preference to a higher mass fragment over a smaller fragment to enable as few overlapping target enhanced functions as possible. Several options were trialed and the windows and masses presented in Figure 2 gave what was deemed as the most acceptable sensitivity over the widest range of compounds. The mass spectra for all target compounds listed in Table 1 are presented in the supporting information 1 (SI 1) along with the retention times and selected ions in supporting information 2 (SI 2). Ionization parameters including; corona voltage, cone gas flow rate and desolvation gas flow rate were all tested to optimize performance. The corona voltage was tested at 3, 5, 7 and 10 mAu, and gas flow rates tested from 75 to 275 L hr^{-1} at intervals of 50 L hr^{-1}. The sensitivity was greatest for the majority of compounds at 5 mAu, with the cone gas flow rate of 175 L hr^{-1} and auxiliary gas flow rate of 175 L hr^{-1}. These parameters are similar to those recorded by van Bavel et al.[24] for APCI analysis of dioxins by tandem mass spectrometery (MS/MS).

Analysis of NIST SRM 2585 by APCI. To test the accuracy of the method the NIST standard reference material SRM2585 – organic contaminants in house dust was extracted and analyzed. Five sub samples of the dust were extracted and analyzed by both APCI-HRqTOFMS and EI-HRMS. There was an excellent correlation between the two datasets (R^2 value of 0.996). Both data sets also compared very favorably with the confidence values provided for the certified PBDEs in the NIST SRM (Figure 1 and Table 3). The relative standard deviation (RSD) of the measurements made using EI- HRMS and APCI-HRqTOFMS were generally within the confidence levels reported by NIST. Both instruments provided more precise measurements for the less brominated PBDEs than the higher brominated congeners (PBDEs 183, 203, 206 and 209). The accuracy of the measurements compared to the NIST values were generally better when using APCI-HRqTOFMS which had an average accuracy for the 14 PBDEs of 109 % compared to 118 % using EI- HRMS. However, when comparing total PBDE values EI- HRMS produced a concentration closer to the NIST value.

The five extracts of NIST SRM 2585 were screened for the presence of the 25 additional emerging HFRs listed in Table 2. For analysis using EI-HRMS this required reanalysis of the sample using a series of different methods, however as the HRqTOFMS was operated in full scan with target enhanced functions there was no need to reanalyze the samples. The target enhanced functions (Table 2) produce an enhanced signal for a range of approximately +/-1.2 multiplied by the selected mass.

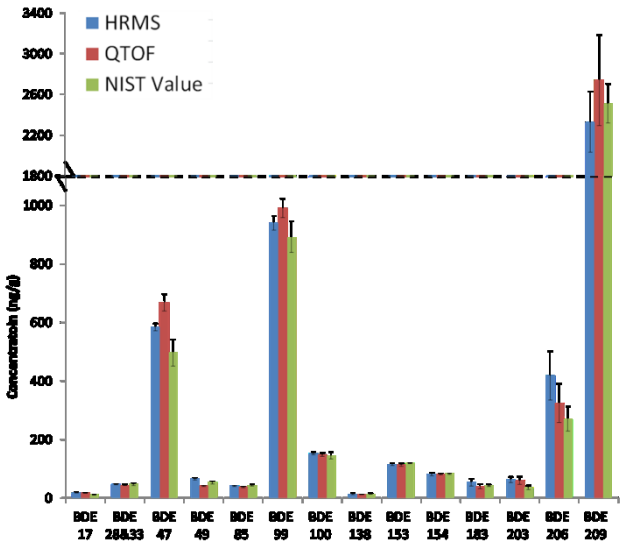

Figure 1. Comparison of EI with HRMS and APCI with HRqTOFMS data with NIST SRM2585 certified values (note staggered scale to include BDE209 values)

As different functions each require a proportion of the total available scan rate it is important to have as few overlapping functions as possible to maintain sensitivity and record the peak shape properly. The functions selected in Table 2 were chosen by plotting the mass of the target ion for each HFR against its retention time (Figure 2). The time windows for each function were kept relatively wide to account for any shifts in retention time that could occur during analysis. As per a classical SIM

based HRMS method the timings for the target enhanced windows were checked by running the CS2 standard at the beginning of each run.

There are currently no certified values for the emerging halogenated flame retardants in NIST SRM 2585, although values for a limited set of HFRs (EHTBB, BTBPE, BEHTBP, DBDPE) have been reported.[25] Ten of the 25 emerging HFRs listed in Table 1 were detected in the dust standard, this included; p-TBX, PBBZ, PBT, PBEB, TDCPP, HBBZ, EHTBB, TBBPA, BEHTBP and BTBPE. The concentrations of these emerging HFRs in the five dust extracts are presented in Table 4. The relative standard deviation for the emerging HFR concentrations was greater than those observed for the PBDEs in most cases. The results were compared against the limited existing data for HFRs in NIST 2585 and showed a good correlation with Stapleton et al.[26] and Lankova et al. [27] but were generally approximately an order of magnitude lower than results reported by Sahlström et al.[25] Ali et al. [28] , Van den Eede et al. [29] and Fan et al. [30]. Fan et al. [30] analyzed 15 HFRs in NIST 2385 and detected ATE, α and β TBECH, and syn and anti DP. This highlights the differences in HFR measurements performed by different groups and increases the importance of studies such as INTERFLAB [31] to monitor performance of flame retardant analysis.

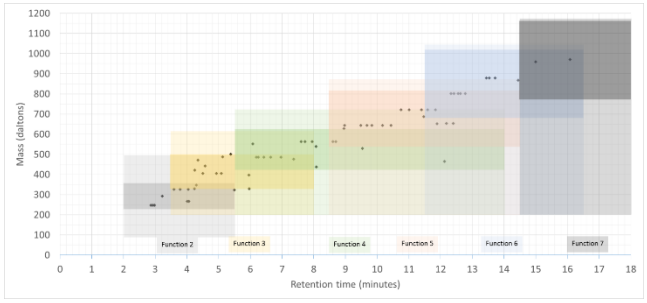

Figure 2. Target enhanced function windows overlaid on a plot of retention time against mass of target ion

Table 3. Comparison of EI-HRMS and APCI-HRqTOFMS data with NIST SRM2585 certified values

	NIST Value			EI-HRMS				APCI- HRqTOFMS			
	Concentration (ng g^{-1})	SD	RSD	Concentration (ng g^{-1})	SD	RSD	Accuracy (%)	Concentration (ng g^{-1})	SD	RSD	Accuracy (%)
BDE 17	11.5	1.20	10.4	18.9	0.617	3.27	164	17.3	1.2	7.1	150
BDE 28&33	46.9	4.40	9.38	47.3	1.96	4.14	101	44.3	1.2	2.8	94.6
BDE 47	497	46.0	9.26	585	12.2	2.09	118	668	28.3	4.2	134
BDE 49	53.5	4.20	7.85	65.4	3.11	4.75	122	42.0	1.4	3.4	78.5
BDE 85	43.8	1.60	3.65	41.7	1.57	3.75	95.3	38.7	2.2	5.7	88.3
BDE 99	892	53.0	5.94	939	24.0	2.55	105	990	32.2	3.3	111
BDE 100	145	11.0	7.59	153	3.14	2.06	105	148	5.9	4.0	102
BDE 138	15.2	2.00	13.2	14.5	2.82	19.5	95.1	13.5	1.0	7.2	88.8
BDE 153	119	1.00	0.84	116	3.02	2.61	97.2	114	4.2	3.7	95.9
BDE 154	83.5	2.00	2.40	82.6	4.99	6.04	98.9	81.7	2.1	2.6	97.8
BDE 183	43.0	3.50	8.14	54.1	12.4	23.0	126	41.2	8.3	20.3	95.7
BDE 203	36.7	6.40	17.4	63.0	9.60	15.2	172	60.4	12.2	20.1	165
BDE 206	271	42.0	15.5	418	83.4	19.9	154	325	66.0	20.3	120
BDE 209	2510	190	7.57	2330	294	12.6	92.8	2740	444.1	16.2	109
ΣPBDE	4770			4930	337	6.83	103	5320	527	9.9	112
Average		26.3	8.51		32.66	8.68	118		43.59	8.63	109

Table 4. Concentrations of emerging HFRs identified in NIST standard 2585

	Concentration in pg g^{-1}							Concentration in ng g^{-1}		
	pTBX	PBBZ	PBT	PBEB	HBBZ	EHTBB	BTBPE	TDCPP	TBBPA	BEHTBP
Sample 1	56.1	358	68.2	1170	522	3780	3360	314	207	105
Sample 2	90.0	415	68.8	1210	1080	5800	7410	406	317	140
Sample 3	71.9	298	62.3	1080	609	4980	6180	294	217	117
Sample 4	66.0	324	54.3	1390	1230	3840	4960	370	227	135

Sample 5	43.4	341	75.2	1040	647	3980	7800	307	174	108
Average	**65.5**	**347**	**65.7**	**1180**	**819**	**4480**	**5940**	**339**	**228**	**121**
SD	17.5	43.8	7.88	136	317	888	1820	48	53	16
RSD (%)	26.7	12.6	12.0	11.5	38.8	19.8	30.6	14.1	23.3	13.1
Sahlström et al. [25]						36000	39000			1300
Ali et al. [28]						40000	32000			652
Stapleton et al. [26]						<30000	<8000			145
Van den Eede et al. [29]						26000	39000			574
Lankova et al. [27]									215	
Fan et al. [30]	<MDL	1600	<MDL	7700	2800	38800	37800			

Conclusions

The method presented here utilizes gas chromatography with atmospheric pressure chemical ionization and detection using a high resolution time of flight mass spectrometer to determine halogenated flame retardants in environmental samples. The method provided a comparable and in many cases better performance than the existing techniques that utilize EI–HRMS, particularly for the higher mass HFRs such as BDE 209 and DBDPE that are often the most problematic to analyze. The method was able to produce sub-picogram detection limits for all HFRs with a molecular weight under 900 Da. The method was validated through the analysis of NIST standard 2585 where the average accuracy for the concentrations of the reported PBDEs was determined to be 109%. The presence of twenty five additional HFRs was also screened for in the dust standard and ten were detected in concentrations above the limits of detection (p-TBX, PBBZ, PBT, PBEB, TDCPP, HBBZ, EHTBB, TBBPA, BEHTBP and BTBPE). All HFRs were determined in one analytical run of less than 18 minutes which makes this a powerful technique for the analysis of halogenated flame retardants.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Full names and mass spectra of all HFRs determined are presented in the supporting information as SI 1 (PDF)

Detection limits, quantification and confirmation ions, and retention times for all HFRs are presented in the supporting information as SI 2 (PDF)

Selected ion chromatograms for all target analytes are presented in the supporting information as SI 3 (PDF)

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All authors have given approval to the final version of the manuscript.

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