Application Brief

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Rapid analysis of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) with Agilent Intuvo 9000 GC/5977B single quadrupole GC/MS system

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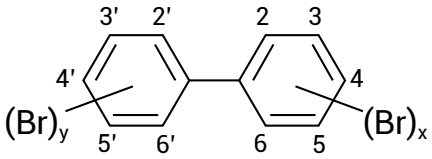
Abstract

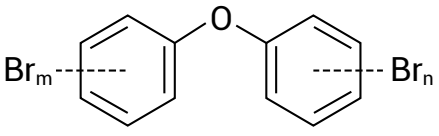
This application note shows a method for rapid analysis of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) with Agilent Intuvo 9000/5977B single quadrupole GC/MS system. The running time of this method is 8.8 min, which is nearly 50% shorter than the that required by the test method described in International Electrotechnical Commission (IEC) standard 62321-6: 2015. The analyzed PBB and PBDE compounds showed good linearity in the concentration range of 0.1 – 5.0 mg/L, with all the correlation coefficients R^2 higher than 0.994. Also the instrument detection limits (IDLs) for various compounds were lower than 15 µg/L.

Introduction

Polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) are common brominated flame retardants. Due to their excellent flame retarding properties, they are used in a wide variety of consumer products, especially electronic appliances. With the obsolescence and disposal of those electrical products, PBBs and PBDEs are introduced into air, water, soil and other cycles as persistent organic pollutants that quickly spread in the environment. Such compounds of very low volatility are difficult to decompose, thus have a long residual period in the environment. They can also be easily accumulated in organisms and human fats, harming the human immune system, brain and nerve tissue, and may even cause cancer. Therefore, the use of PBBs and PBDEs has gained increasing awareness in many countries/regions.



PBB



PBDE

On January 27, 2003, the European Union officially issued the "Waste Electrical and Electronic Equipment Directive" (WEEE-2002/96/EC) [1] and the "Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment" (RoHS-2002/95/EC) [2]. Since July 1, 2006, electrical and electronic products specified by the WEEE directive are required to be free of hazardous substances such as PBBs and PBDEs listed in the RoHS directive when entering the European market. China has formally implemented a new version of the "Administrative Measures on the Control of Pollution Caused by Electronic Information Products" (China RoHS 2.0) on July 1, 2016, which also requires that the content of PBBs and PBDEs in electrical and electronic products must be less than 0.1%.

At present, the detection methods of PBBs and PBDEs are mainly based on the Chinese national standard GB/T 26125-2011 "Electrical and electronic products - Determination of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)" and IEC standard 62321-6:2015 [3]. Both standards employ the gas chromatography-mass spectrometry (GC-MS) system for the analysis of PBBs and PBDEs. However, both types of compounds are prone to debromination and degradation under heat. One example is decabromodiphenyl ether (deca-BDE), which is widely used in industry and can be easily degraded into nonabromodiphenyl ether and octabromodiphenyl ether when heated. Therefore, chromatographic columns with shorter length and thinner film are applied together with a method featuring a faster heating rate in the analysis to reduce the retention time of deca-BDE in the chromatographic column, thus reducing debromination and degradation. For instance, in IEC 62321-6: 2015[3], columns with a length of 15 m, an inner diameter of 0.25 mm, and a film thickness of 0.1 µm are used to analyze PBBs and PBDEs at a temperature ramp rate of 40°C/min. The running time required is 16.25 min.

The new Intuvo 9000 GC system features a direct column heating technology. The system has the advantage of a higher heating rate compared with the traditional GC systems that use air bath for column-heating, thus facilitating the rapid analysis of PBBs and PBDEs. This application note shows a method for rapid analysis of PBBs and PBDEs developed using Intuvo 9000 GC/5977B single quadrupole GC/MS system.

Experiment

Standards and Reagents

The pure standards of PBBs and PBDEs used in this application note were purchased from AccuStandard. The GR grade toluene was purchased from Merck. 10 mg of each standard (0.01 mg precision) was weighed accurately and dissolved in toluene. The solution volume was made up to 10 mL to prepare a single standard stock solution with a concentration of 1000 mg/L. 100 µL of each single standard stock solution was then diluted to reach a volume of 10 mL with toluene to obtain a mixed intermediate solution with a concentration of 10 mg/L.

Instrumentation

Intuvo 9000 GC/5977B single quadrupole GC/MS system was used in this application note, which was operated in the Selected Ion Monitoring Mode (SIM) and Electron Impact Ionization (EI). Inert Plus was applied as the ion source, with a 6 mm drawout lens.

GC conditions

Column	Agilent DB-5HT, 15 m × 0.25 mm × 0.1 µm
Injection mode	Pulsed splitless with an injection volume of 1 µL
Injection port temperature	280 °C
Liner	Single taper, 4 mm ID, without glass wool
Carrier gas	Helium, constant at 1.2 mL/min
Oven temperature program	The temperature was kept at 100 °C for 1 min, and was then increased to 340 °C at a rate of 50 °C/min, which was kept for 3 min.
Transfer line temperature	340 °C
Guard Chip Temperature	Track Oven
Bus Temperature	280 °C

MS Conditions

Ion lens	6 mm
Solvent delay	2 min
Ion sources	EI
Acquisition mode	SIM
Tune File	Atune.u
Source temperature	350 °C
Quadrupole temperature	150 °C
Acquisition parameters	shown in Table 1

Table 1. Acquisition parameters of PBBs and PBDEs.

Compound	RT	Group	Gain factor	Quant ion	Qual ion
Monobromobiphenyl	2.821	1	0.5	232	234, 152
Monobromodiphenyl ether	3.128	1	0.5	248	250, 141
Dibromobiphenyl	3.519	2	0.5	312	152, 310
Dibromodiphenyl ether	3.835	2	0.5	328	326, 168
Tribromobiphenyl	3.928	2	0.5	390	292, 230, 151
Tribromodiphenyl ether	4.337	3	1	406	408, 248
Tetrabromobiphenyl	4.42	3	1	389	310, 470, 150
Pentabromobiphenyl	4.736	3	1	469	388, 548, 550
Tetrabromodiphenyl ether	4.876	3	1	485.8	487.8, 325.9
Hexabromobiphenyl	5.024	3	1	627.7	467.8, 308, 466
Pentabromodiphenyl ether	5.164	3	1	563.7	565.7, 403.8, 406
Hexabromodiphenyl ether	5.768	4	1	483.8	643.7, 481.8
Heptabromobiphenyl	5.815	4	1	626.7	705.8, 547.7, 385.8
Heptabromobiphenyl ether	5.963	4	1	561.7	563.7, 723.7
Octabromobiphenyl ether	6.233	4	1	641.7	639.7, 801.6, 320.8
Octabromobiphenyl	6.289	4	1	785.6	704.6, 465.7, 625.7
Nonabromodiphenyl	6.633	5	2	863.5	784.6, 705.6, 545.7
Nonabromobiphenyl ether	6.856	5	2	721.6	879.6, 719.6
Decabromobiphenyl	7.042	5	2	943.5	783.5, 623.6
Decabromodiphenyl ether	7.627	6	3	799.5	959.5, 797.6

Preparation of mixed standard solutions

The mixed intermediate solutions of PBBs and PBDEs were sequentially diluted with toluene to obtain mixed standard solutions with concentrations of 0.1, 0.2, 0.5, 1.0, 2.0, and 5.0 mg/L, respectively.

Results and Discussion

Fast separation with Intuvo

The Intuvo 9000 GC system used in this application note is equipped with direct column heating features. The column oven can be heated from 100 °C to 340 °C at a rate of 50 °C/min, which is greatly improved compared with the traditional gas chromatography system that heats columns via air bath. Figure 1 shows the overlaid total ion currents (TIC) chromatograms of mixed PBBs and PBDEs standard solutions at 6 concentration levels, including 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 mg/L. 20 PBB and PBDE compounds were all eluted within 8 min with a great resolution. Compared with the analysis time of 16 min listed in the IEC 62321-6:2015 standard (see Figure 2), the analysis efficiency was doubled and the sample throughput was significantly increased.

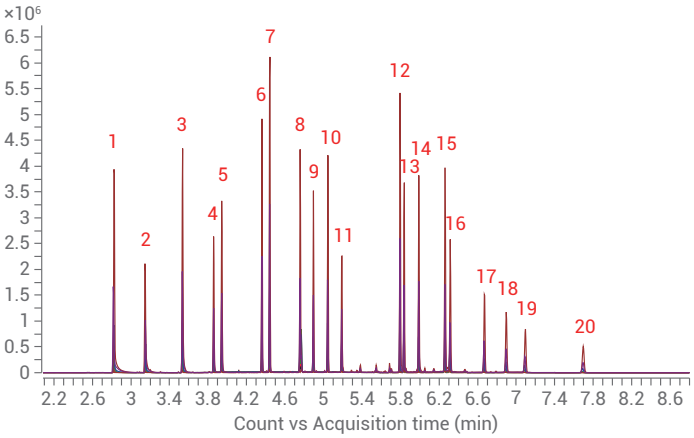


Figure 1. Overlaid total ion current chromatograms (TIC) of PBB and PBDE mixed standard solutions at 6 concentration levels: 1. Monobromobiphenyl; 2. Monobromodiphenyl ether; 3. Dibromobiphenyl; 4. Dibromodiphenyl ether; 5. Tribromobiphenyl; 6. Tribromodiphenyl ether; 7. Tetrabromobiphenyl; 8. Pentabromodiphenyl; 9. Tetrabromodiphenyl ether; 10. Hexabromodiphenyl; 11. Pentabromodiphenyl ether; 12. Hexabromodiphenyl ether; 13. Heptabromodiphenyl ether; 14. Heptabromodiphenyl ether; 15. Octabromodiphenyl ether; 16. Octabromodiphenyl; 17. Nonabromodiphenyl; 18. Nonabromobiphenyl ether; 19. Decabromodiphenyl; 20. Decabromodiphenyl ether.

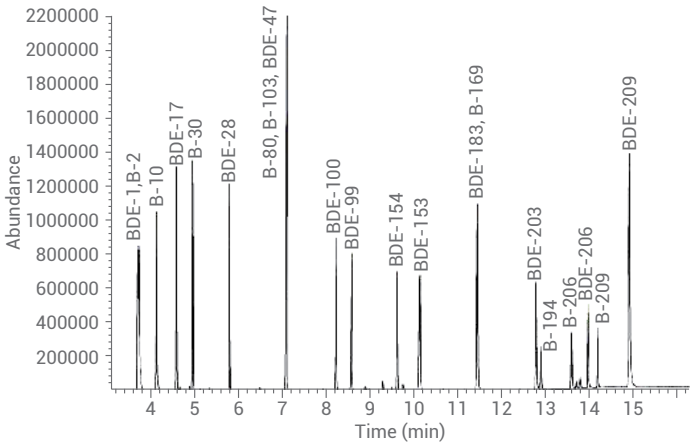


Figure 2. Overlaid TICs of PBB and PBDE compounds in IEC 62321-6:2015 [3].

Linearity

Mixed standard solutions with concentrations of 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0 mg/L were analyzed, based on which a calibration curve was created. Table 2 lists the linear ranges and correlation coefficients of 20 PBB and PBDE compounds. Among them, except for nonabromodiphenyl ether and decabromodiphenyl ether with a linear range of 0.2-5.0 mg/L, the other 18 compounds all showed a great linearity of 0.1-5.0 mg/L, and the correlation coefficients of all compounds R^2 were ≥ 0.994.

Table 2 Linear ranges and correlation coefficients of 20 PBB and PBDE compounds.

Chemical	Linear range (mg/L)	Linear equation	Correlation coefficient (R^2)
Monobromobiphenyl	0.1-5	Y = 222651.35X + 9032.51	0.996
Monobromodiphenyl ether	0.1-5	Y = 137845.64X + 4680.94	0.997
Dibromobiphenyl	0.1-5	Y = 223963.81X + 7740.18	0.996
Dibromodiphenyl ether	0.1-5	Y = 168872.52X + 68773.32	0.994
Tribromobiphenyl	0.1-5	Y = 137213.72X + 5755.34	0.996
Tribromodiphenyl ether	0.1-5	Y = 193443.08X + 7610.94	0.994
Tetrabromobiphenyl	0.1-5	Y = 103108.77X + 2703.44	0.997
Pentabromobiphenyl	0.1-5	Y = 129205.14X + 2960.67	0.997
Tetrabromodiphenyl ether	0.1-5	Y = 183662.50X + 5218.22	0.995
Hexabromobiphenyl	0.1-5	Y = 115377.77X + 1579.74	0.999
Pentabromodiphenyl ether	0.1-5	Y = 97392.08X + 2034.85	0.996
Hexabromodiphenyl ether	0.1-5	Y = 293661.54X + 4839.26	0.997
Heptabromobiphenyl	0.1-5	Y = 60220.16X + 1961.89	0.999
Heptabromobiphenyl ether	0.1-5	Y = 168381X + 788.76	0.995
Octabromobiphenyl ether	0.1-5	Y = 144478.61X + 12592.09	0.997
Octabromobiphenyl	0.1-5	Y = 102265.13X + 4994.27	0.998
Nonabromodiphenyl	0.1-5	Y = 94644.96X + 14880.90	0.997
Nonabromobiphenyl ether	0.2-5	Y = 102302.97X + 16975.61	0.998
Decabromobiphenyl	0.1-5	Y = 74510.80X + 16652.98	0.995
Decabromodiphenyl ether	0.2-5	Y = 70342.76X + 14949.15	0.996

Reproducibility

The mixed standard solution of 0.1 mg/L PBBs and PBDEs was continuously analyzed for 8 times to evaluate the reproducibility of the method described in this application note. Figure 3 shows the overlaid chromatograms of the quantifier ions of the 20 compounds. It can be seen from the figure that even at the lowest concentration point of the calibration curve, the retention time of the compounds and the response of the chromatographic peaks showed great repeatability. The relative standard deviations (RSD) of the analysis results were all < 6% (see Table 3), indicating an impressive reproducibility of the method.

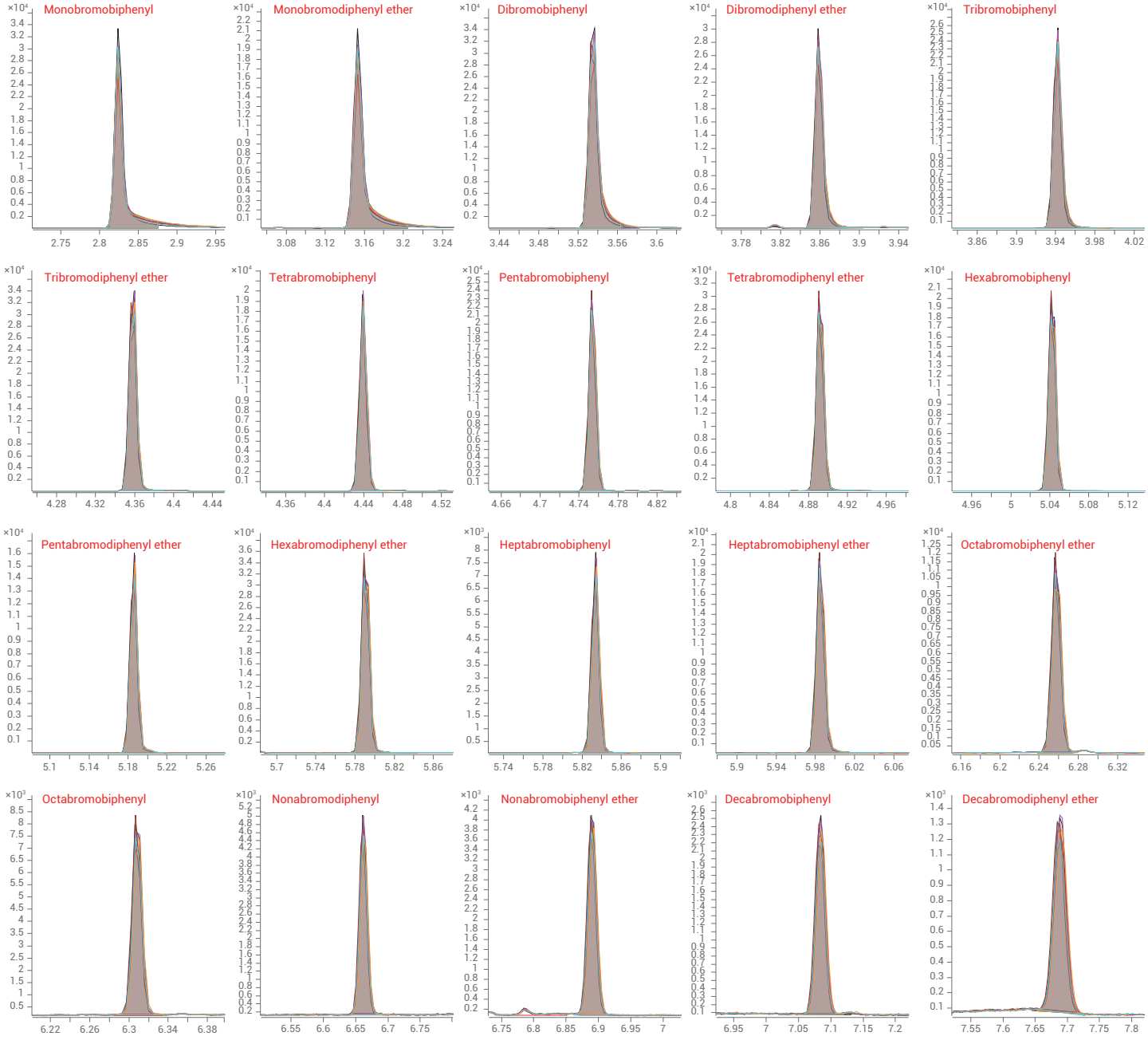


Figure 3. Overlaid quantifier ion chromatograms of various compounds obtained from a consecutive analysis of 0.1 mg/L mixed standard solution for 8 times.

Table 3. Relative standard deviations (RSD) of various compounds obtained from a consecutive analysis of 0.1 mg/L mixed standard solution for 8 times.

Compound	RSD
Monobromobiphenyl	5.28%
Monobromodiphenyl ether	5.21%
Dibromobiphenyl	5.26%
Dibromodiphenyl ether	5.02%
Tribromobiphenyl	5.06%
Tribromodiphenyl ether	5.00%
Tetrabromobiphenyl	4.80%
Pentabromobiphenyl	4.68%
Tetrabromodiphenyl ether	4.86%
Hexabromobiphenyl	4.86%
Pentabromodiphenyl ether	4.99%
Hexabromodiphenyl ether	5.26%
Heptabromobiphenyl	5.47%
Heptabromobiphenyl ether	5.09%
Octabromobiphenyl ether	5.45%
Octabromobiphenyl	4.97%
Nonabromodiphenyl	5.32%
Nonabromobiphenyl ether	5.20%
Decabromobiphenyl	5.09%
Decabromodiphenyl ether	5.25%

Table 4. RSDs and calculated IDLs for 8 consecutive measurements of 0.05 mg/L mixed standard solution

Compound	RSD	IDL (µg/L)
Monobromobiphenyl	4.12%	6.2
Monobromodiphenyl ether	3.20%	4.8
Dibromobiphenyl	2.71%	4.1
Dibromodiphenyl ether	2.68%	4.0
Tribromobiphenyl	2.53%	3.8
Tribromodiphenyl ether	3.62%	5.4
Tetrabromobiphenyl	3.77%	5.6
Pentabromobiphenyl	3.94%	5.9
Tetrabromodiphenyl ether	4.43%	6.6
Hexabromobiphenyl	4.11%	6.2
Pentabromodiphenyl ether	6.29%	9.4
Hexabromodiphenyl ether	6.29%	9.4
Heptabromobiphenyl	5.96%	8.9
Heptabromobiphenyl ether	7.57%	11.3
Octabromobiphenyl ether	7.21%	10.8
Octabromobiphenyl	7.18%	10.8
Nonabromodiphenyl	8.56%	12.8
Nonabromobiphenyl ether	9.43%	14.1
Decabromobiphenyl	7.75%	11.6
Decabromodiphenyl ether	9.19%	13.8

Instrument detection limit

The instrument detection limit (IDL) refers to the minimum concentration or content of the analyte detectable by an analytical instrument under the same analytical conditions as the sample determination, without the presence of a sample matrix or influences of any sample preparation steps. IDL corresponds to the smallest response signal distinguishable by the instrument from background noise, base on the calculation formula below:

$$IDL = t_{\alpha,n} \times RSD \times \text{standard sample concentration/content}$$

In this application, a mixed standard solution of PBBs and PBDEs with a concentration of 0.05 mg/L was used as the IDL test solution, and 8 consecutive tests were performed. Using the degrees of freedom n = 7, and α = 0.01 (the confidence interval is 99%) in the above calculation formula, $t_{\alpha,n}$ = 2.998 was obtained from the t distribution table. The IDL results for various PBB and PBDE compounds can thus be calculated as listed in Table 4. From the results, it can be seen that the IDLs of all compounds are lower than 15 µg/L, which fully meets the method performance requirements of IEC 62321-6: 2015.

Conclusions

This application note shows a method for rapid analysis of PBBs and PBDEs established with Intuvo 9000 GC/5977B single quadrupole GC/MS system. This method takes the advantage of the direct column heating technology of the Intuvo 9000 GC system to improve the heating rate. The analysis of 20 PBB and PBDE compounds can be completed in 8.8 min, which is only around half that of the method described in IEC 62321-6: 2015. The method also showed excellent accuracy, reproducibility and sensitivity. The compounds analyzed all showed great linearity in the concentration range of 0.1–5.0 mg/L, with the correlation coefficients R2 higher than 0.994. The instrument detection limits for various compounds were all lower than 15 µg/L, meeting the requirements of IEC 62321-6: 2015.

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