

ANALYSIS OF CONTAMINATED PBDES IN SEDIMENT SAMPLES USING THE TRIPLE QUADRUPOLE GC/MS/MS

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TÓM TẮT

PHÂN TÍCH HÀM LƯỢNG PBDE TRONG CÁC MẪU TRẦM TÍCH SỬ DỤNG PHƯƠNG PHÁP GC/MS/MS 3 KHỐI TỬ CỰC

Bài báo trình bày kết quả phát triển phương pháp phân tích các hợp chất PBDE dựa trên phương pháp EPA 1614, sử dụng sắc ký khối phổ 3 lần tử cực GC/MS/MS. Kết quả cho thấy phương pháp có độ chính xác cao, độ thu hồi cao từ 78 đến 110 %, đáp ứng các yêu cầu của phân tích vết. Đặc biệt giá trị LOD của thiết bị phân tích đối với các PBDE rất thấp, dao động trong khoảng từ 9.9-41.3pg/ μ L và LOQ từ 33.0-137.7pg/ μ L, rất phù hợp để áp dụng vào phân tích PBDE trong các mẫu có hàm lượng nhỏ. Kết quả phân tích PBDE trong các mẫu trầm tích lấy ở một số sông hồ ở Hà Nội như hồ Yên Sở, Đền Lừ, và sông Tô Lịch phát hiện thấy trong các mẫu này, BDE-99 chiếm hàm lượng nhiều nhất, sau đó đến BDE-47 và BDE-100. Tổng nồng độ của PBDE trong các mẫu này tương đối nhỏ (từ 0.007ng/g đến 1.046 ng/g khô) so với các nghiên cứu khác trong khu vực, cho thấy mức độ ô nhiễm PBDE ở Hà Nội vẫn còn nằm ở mức thấp.

1. INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are anthropogenic chemicals that have been extensively used as flame-retardants. The compounds are incorporated into many types of polymers used in electric circuit boards of

computer and television housings, furniture, building materials, textiles, carpets and vehicles. The concern over PBDEs is increasing due to their persistent and bioaccumulative properties and potential toxic risk to humans. Various PBDEs have been detected with

significant levels in environmental matrices such as air^[1,2], sediment^[3,4,5], and sewage sludge^[6] as well as in biological samples including biota, human blood, adipose tissues and breast milk. As the predicted consumption of BFRs in future may increase in connection to the rapid industrialization in Asian developing countries, the demand for monitoring of pollution by PBDEs is necessary. There are few investigations on PBDEs in some cities and industrial areas in Vietnam^[7,8]. The level of PBDE contamination in sediments in several places in Northern Vietnam has been assessed, however PBDEs are detected only at highly contaminated places such as e-waste villages at Bui Dau, Hung Yen but not at urban places like Hanoi since the PBDE level lies below the LOD of the used analysis method.

In order to evaluate the PBDE contamination due to urban industrialization activities, an analysis method with higher sensitivity and much lower LOD hence is needed. Our objectives in this article is to develop a method based on EPA 1614 using triple quadrupole GC/MS/MS and apply to analyze PBDE in sediment samples

collected from rivers and lakes in Hanoi.

2. EXPERIMENTAL

2.1. Chemicals and instruments

- Both native and ¹³C-labeled standard solution of PBDEs were purchased from Cambridge Isotope Laboratories (Massachusetts, United States). Organic solvents and others chemical were at least analytical grade.

- Instrument Agilent 7000 triplequadrupole, USA and DB-5MS (60m x 250µm i.d x 0.25 µm film thickness) capillary column.

2.2 Sampling and storage

The sediment samples were collected in To Lich river, Nhue river, Kim Nguu river, Lu river, Set river, Tuong Mai lake and Yen So lake. The samples were collected using Ekman Grab sampler on the surface layer (1-20cm). Samples at rivers were collected at points that located near river banks. After being homogenized, about 200g of sample was taken out, poured in a clean, opaque glass jar and stored at -10⁰C in darkness.

2.3. Method of analysis

The analytical procedure of PBDEs in soil/sediment samples on GC/MS/MS instrument is modified on the basis of method EPA 1614 and is summarized in Fig.

1.

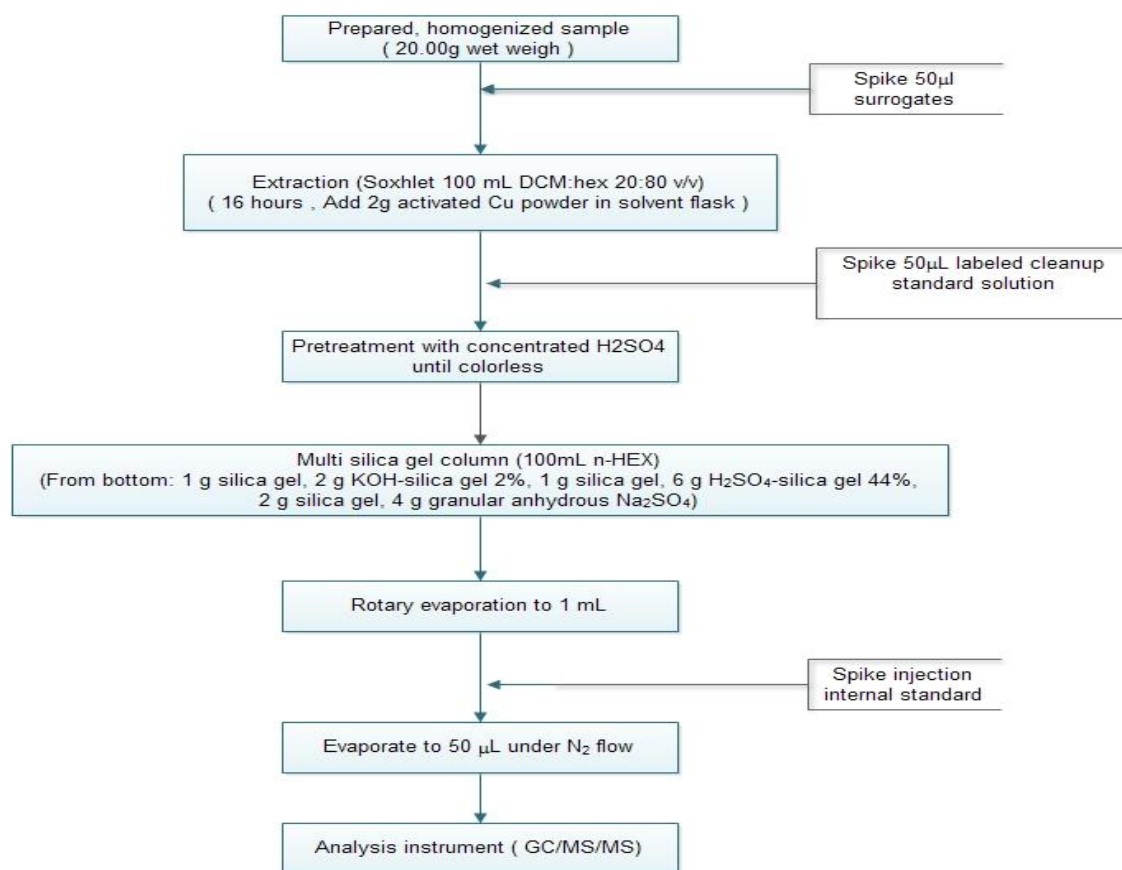


Figure 1. Flowchart of modified method EPA 1614

2.4. GC/MS/MS analysis

Samples were analyzed on GC/MS/MS instrument with the following programs: GC running program: Initial temperature: 88°C, hold time 5min, increase 600°C/min from 80°C to 325°C, remain at 325°C until finishing; sample volume: 1.0±0.2µl; support gas capacity of He: 1.8 mL/min; chromatography column, J&W 121-5822 (DB-5) Agilent (20m × 0.18mm; film thickness of 0.18µm); Oven temperature: 90°C, hold time 1min, increase 20°C/min from 90°C to 320°C, remain at 320°C until

finishing; Thermal auxiliary: 300°C. The mass spectrometer was operated with electron impact ionization (EI) mode at source temperature of 350°C and electron energy of 70eV. Mass spectrometer 1 temperature: 150°C Mass spectrometer 2 temperature: 150°C. Mass selective detector (MSD) was operated by selecting ion monitoring (SIM) for typical ions of each BDE.

2.5. Quality assurance and quality control

The quality assurance and quality control (QA/QC) samples included solvent blanks, matrix blank and spiked matrix,

all of which were analyzed together with the collected sediment samples. Sodium sulfate was used for the matrix blank and matrix spiked samples. Ten nanograms of native PBDEs standard mixture were spiked into 20g of sodium sulfate to prepare the matrix-spiked samples for evaluation of method performance. Relative errors and standard deviation obtained from analyzing 3 matrix-spiked samples were used to evaluate the accuracy and precision.

3. Results and discussion

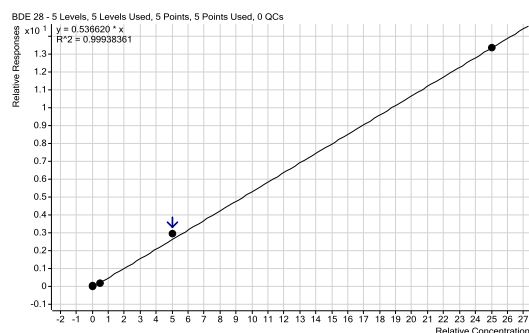


Figure 2. Calibration curves of BDE-28

All calibration curves of 7 congeners of PBDEs had relatively high relationship of linearity with the R^2 all larger than 0.99 (see Fig.2,3 for calibration curves of BDE-28 and BDE-48). LOD values calculated from calibration curves range from 9.9-41.3 pg/ μ L while LOQ values vary from 33.0-137.7pg/ μ L. The very low values of LOQ indicate that the method is very suitable for the determination of PBDE congeners with

3.1. Validation of the analytical method

3.1.1. Calibration curves, LOD and LOQ of PBDE congeners

Determination of PBDEs was based on retention time and fragment of typical ions. The quantization of PBDEs was conducted through establishment of calibration curves, which expresses the area or height of peak versus the concentration of analytes and includes five points with concentrations in the range from 1 to 2500 ng/mL.

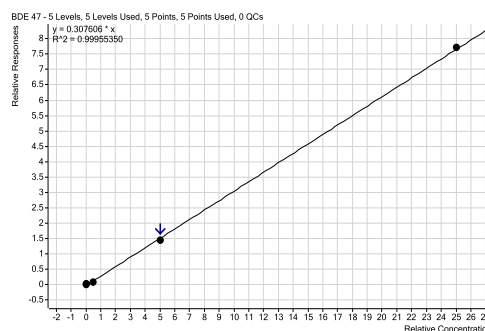


Figure 3. Calibration curves of BDE-48

low concentrations, for example, in the sediment samples.

3.1.2. Accuracy of the analytical method

The accuracy of a method is evaluated based on two criteria: precision and trueness, which are represented by RSD and recovery, respectively. The recovery and RSD of spiked native BDEs samples on Na₂SO₄ matrix was evaluated and represented in Table 1.

Table 1. Recovery and RSD of spiked native BDEs samples on Na₂SO₄ matrix

Congeners	BDE- SPK 1-2	BDE- SPK 2-2	BDE- SPK 3-2	Average found (pg/uL)	Spiked (pg/uL)	%Recov ery	%RSD
BDE-28	250.0	227.6	180.0	219.2	200	110	16.3
BDE-47	230.0	211.7	196.0	212.6	200	106	8.0
BDE-100	213.7	210.7	207.0	210.5	200	105	1.6
BDE-99	208.6	205.7	202.1	205.5	200	103	1.6
BDE-154	204.7	203.7	199.7	202.7	200	101	1.3
BDE-153	149.4	120.0	198.6	156.0	200	78	25.5
BDE-183	207.4	213.4	205.3	208.7	200	104	2.0

The RSD values of most congeners were in the good range from 1,3 to 8%. Some congeners (BDE-28, BDE-153) have higher RSD but still in the acceptance error range of measurement (RSD<40%). Recovery ranged from 78-110% which is in the acceptable range (60-140%). Hence, this method can be applied well to determine the concentration of PBDEs in sediment samples.

3.2. Determination and assessment of concentrations of PBDEs in sediment samples collected in rivers and lakes of Hanoi

The analysis of sediment samples in 3 sampling sites (Yen So lake, denoted as YS1, YS2, YS3; Den Lu lake, denoted as DL1, DL2; To Lich river, denoted as TL4, TL5) was performed. Applying the modified method EPA 1614, the analytical results are given in Table 2

Table 2. PBDE concentrations of 7 real samples (pg/g, wet weight)

Name	11HN- YS 1	11HN- YS2	11HN- YS3	11HN- DL1	11HN- DL2	11HN- TL5	11HN- TL4
BDE-28	1.5	1.6	8.5	1.8	ND	2.1	ND
BDE-47	86.0	100.5	181.8	18.6	10.3	59.9	11.5
BDE-100	21.5	42.2	29.7	3.3	2.0	17.6	1.9
BDE-99	174.2	259.7	340.1	24.9	9.7	99.5	14.2
BDE-154	15.7	22.0	25.2	3.8	6.5	10.5	ND
BDE-153	18.2	29.2	71.8	4.3	3.1	24.9	2.7
BDE-183	ND	ND	91.6	ND	ND	18.8	ND
Total PBDEs	317.2	455.2	748.7	56.7	31.6	233.3	31.9

Not all of the BDE congeners were detected in sediment samples. BDE-183 can only be detected in 2 samples at different reservoirs. BDE # 99 is the predominant congener (accounted for about 50% of the total PBDEs), followed by BDE #47 (35%) and BDE #183 (5%). The predominance of low-brominated PBDE (BDE-47, 99, 100) were also found in sediments of other studies [2,3], especially in Thi Nai lagoon, Vietnam [7]. However, in Thi Nai sediments the presence of BDE-153 was detected, but not at all sites, and with low percentage. The congener profile of sediments in Hanoi reveals that PBDE congeners may come from both penta-BDE and octa-BDE mixtures, and be released from different sources and through a number of pathways including atmospheric emissions, recycling of wastes containing PBDEs, volatilization from consumer products, and leaching from disposal sites,...

The total PBDE concentrations in sediments, ranged from 738.64 to 1046.73pg/g (dry wt) in Yen So Lake, 74.37 to 133.95pg/g (dry wt) in Den Lu Lake and 104.16 to 584.31pg/g (dry wt) in To Lich River. The descending order of PBDEs was Yen So Lake > Den Lu Lake > To Lich river. For samples of Yen So Lake, all of BDE congeners have abnormal high concentration in comparison with other samples, giving an evidence of a emerging source that

releases a high amount of PBDEs into Yen So Lake. At Yen So Lake and Den Lu Lake, different locations of the same station share a similar concentration of congeners. In To Lich River, the concentration of all congeners in sample TL5 are 3 – 10 times higher than that of TL4 sample. One of the possible reasons for this difference is the presence of releasing sources that affect only TL5 but not TL4 location. However, the total concentrations of PBDEs in all sampling sites are relatively small in comparison with other places in the world, indicating that the PBDEs contamination status in Hanoi is not at a high level.

4. CONCLUSIONS

The modified method EPA 1614 suit requirements for analysis of PBDEs with good precision and high recovery ranging from 78-110%. LOD values of the method range from 9.9-41.3pg/ μ L while LOQ values vary from 33.0-137.7pg/ μ L. The method was applied well to analyse PBDE in sediment samples collected in Yen So lake, Den Lu lake and To Lich river. Results show that the pattern profiles of PBDEs in 3 sampling sites are similar with each other whereas BDE-99 is the predominant, follow by BDE-47 and BDE-100. The total concentrations of PBDEs in 3 sampling sites are relatively small in compare with other studies, indicating that the PBDEs contamination status in Hanoi is not at a high level. We hope that in the future,

this method can be applied for PBDE analysis in soil and biological samples. As a result, the transport and bio-accumulation of PBDEs in the lake and river system of Hanoi can be evaluated for an efficient treatment method for PBDEs contaminated areas.

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