Migration and Transformation Rules of Brominated Flame Retardants During the Pyrolysis of Electronic Waste

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Abstract: ***To explore the migration and transformation rules of brominated flame retardants (BFRs) during the pyrolysis of electronic waste, ABS casings containing PBDEs and TBBPA, brominated epoxy resin motherboards, and HIPS toy parts were selected. Using a fixed-bed pyrolysis system and GC-MS/MS analysis, the effects of pyrolysis temperature and material were observed. With the increase in temperature, the total migration rate of BFRs increased from 15%~25% at 300°C to over 90% at 700°C, and the proportion of gaseous products rose; PBDEs mainly underwent debromination reactions, while TBBPA underwent both debromination and ether bond cleavage; The migration rate of PBDEs in ABS materials. was relatively high, the conversion rate of TBBPA in motherboards was low, and metal impurities could promote debromination.***

Keywords: Electronic waste pyrolysis; Brominated flame retardants; Migration rules; Transformation pathways; Material influence.

1. INTRODUCTION

Electronic waste has become one of the fastest-growing solid wastes globally, with about 2.4 million tons generated annually in China. Its improper disposal can produce toxic and harmful substances, posing a serious threat to the environment and human health. If electronic waste can be properly treated, it can not only reduce pollution to the ecological environment but also achieve resource recycling. When brominated flame retardants (polybrominated diphenyl ethers, tetrabromobisphenol A) are pyrolyzed, their migration and transformation behaviors are directly related to the risk of secondary pollution and the efficiency of resource recovery. By selecting typical bromine-containing electronic waste, the effects of pyrolysis temperature and material characteristics on the migration rate and transformation pathways of brominated flame retardants are studied, and their migration and transformation rules are revealed to provide a scientific basis for pollution control during the pyrolysis of electronic waste [1-3]. Wang and Lai (2026) proposed an innovative approach to enhance upper-room ultraviolet germicidal irradiation (UVGI) performance by employing a rotating UV source under poorly-mixed ventilation conditions, which could improve disinfection efficiency in real indoor environments [4]. Narouei et al. (2025) investigated the effects of germicidal far-UVC on ozone and particulate matter in a conference room, revealing that far-UVC irradiation can significantly affect secondary chemical reactions and aerosol dynamics [5]. Sun (2024) conducted research on modification and screening of antibiotic-producing strains, demonstrating effective methodologies to increase antibiotic yields through strain improvement [6]. Bang et al. (2025) experimentally evaluated the disinfection performance of far-UVC at 222 nm in residential spaces, using Bacillus subtilis contamination to show its efficacy in reducing bacterial load under practical conditions [7]. Xiao et al. (2022) developed an ultrasmall Fe_3O_4-decorated polydopamine hybrid nanozyme that enables continuous conversion of oxygen into toxic hydroxyl radicals via glutathione-depleted cascade redox reactions, and they applied this system for intensive wound disinfection with promising therapeutic outcomes [8].

2. MATERIALS AND METHODS

2.1 Reagents and Materials

The brominated flame retardant standards used in the experiment include polybrominated diphenyl ethers (PBDEs, including 7 homologues such as BDE-28 and BDE-47) and tetrabromobisphenol A (TBBPA), with purity ≥ 98%, purchased from AccuStandard; chromatographic pure n-hexane and dichloromethane were purchased from Tedia; e-waste samples were from a treatment center, including waste LCD TV casings (ABS material, bromine content 4.1% - 6.3%), laptop computer motherboards (brominated epoxy resin, bromine content 9.2% - 11.8%), and children's toy plastic parts (HIPS material, bromine content 2.5% - 3.8%). Three brand batches of each were taken, 300 g per batch, sealed in a polytetrafluoroethylene bag and stored at 4 °C refrigerated. For pretreatment,

anhydrous sodium sulfate was calcined at 450°C for 4 h, and silica gel with a mesh size of 100 - 200 was activated at 130 °C for 12 h and placed in a desiccator for standby.

2.2 Instruments and Equipment

A triple quadrupole gas chromatography-mass spectrometer (Thermo Scientific TSQ Quantum XLS Ultra) equipped with a DB-5MS capillary column ($30\ m \times 0.25\ mm \times 0.25\mu m$) was selected to achieve baseline separation of PBDE congeners and TBBPA. A fixed-bed pyrolysis system was used for the pyrolysis experiment to accurately simulate the pyrolysis conditions. The condensation collection device consisted of a double-layer glass condenser and a 500 mL collection bottle, and an ice-water bath ($0 \sim 5°C$) was used for efficient condensation of liquid tar. Subsequently, the adsorption tube was filled with glass wool of 60-80 mesh, and the interception rate of semi-volatile brominated flame retardants was over 95%. A mixed solution of n-hexane-dichloromethane with a volume ratio of 1:1 in the absorption bottle was used to capture gaseous flame retardants with an efficiency of over 90%. For sample pretreatment, an electronic balance BSA224S with a range of 0-220 g and an accuracy of 0.1 mg was used; a high-speed centrifuge TGL-16M could centrifuge at 4000 r/min for 10 min to completely precipitate impurities; an ultrasonic cleaner AS3120 300 W was used to accelerate the dissolution of flame retardants, and the extraction efficiency was increased by more than 30% compared with the traditional method.

2.3 Experimental Methods

1) Preparation of standard solutions. For PBDEs, a mixed standard of 7 target compounds including BDE-28 and BDE-47 was selected. Weigh 10.0 mg and place it in a 10 mL brown volumetric flask. Add a mixed solvent of n-hexane and dichloromethane (volume ratio 1:1) to dissolve and make up the volume to prepare a $1000\mu g/mL$ mixed stock solution. For TBBPA, weigh 10.0 mg of pure product separately and dissolve and make up the volume to 10 mL in the same way to prepare a $1000\mu g/mL$ single standard stock solution. When in use, pipette an appropriate amount of solution from the stock solution and dilute it step by step with n-hexane to prepare a mixed standard working solution with PBDEs series concentrations of 0.1ng/mL, 0.5ng/mL, 1ng/mL, 5 ng/mL, 10 ng/mL, 50 ng/mL, 100 ng/mL, and a single standard working solution with TBBPA series concentrations of 0.5ng/mL, 1ng/mL, 5 ng/mL, 10 ng/mL, 20 ng/mL, 50 ng/mL, 100 ng/mL. Prepare and use immediately.

2) Pyrolysis experimental conditions. Weigh 10.0 g of the e-waste sample that has been ground and sieved (particle size controlled at $0.5 \sim 1$ mm), and evenly spread it in the quartz boat in the middle of the quartz reaction tube. Place the reaction tube horizontally in a programmed temperature tube furnace, seal both ends with silica gel plugs, connect the gas pipeline and introduce high-purity nitrogen (purity 99.999%), adjust the flow rate to 50 mL/min, and continuously purge for 30 min. Set the furnace heating program: the initial temperature is maintained at room temperature, and then it is uniformly heated to the preset pyrolysis temperature (300°C 、 400°C 、 500°C 、 600°C 、 700°C) at a rate of 10°C/min, and keep it at a constant temperature for 30 min after reaching the target temperature. During this period, the nitrogen purge rate is stably controlled by a mass flow meter. The mixed products generated by pyrolysis are led out through a quartz conduit and enter a three-stage collection device in sequence: the first stage is a 50 mL pear-shaped flask placed in an ice-water bath, which is used to condense and collect the liquid tar components; the second stage is a glass adsorption tube filled with 10 g pretreated glass wool to intercept semi-volatile organic compounds; the third stage is an absorption bottle containing a 50 mL n-hexane-dichloromethane mixed solvent (volume ratio 1:1), and gaseous organic compounds are absorbed by bubbling.

3) Sample pretreatment. For liquid tar samples, weigh 1.0000 g and place it in a 50 mL stoppered centrifuge tube. Add 10 mL of a n - hexane - dichloromethane mixture (volume ratio 1:1), ultrasonically extract for 30 min at 300 W power, then centrifuge at 4000 r/min rpm for 10 min. Pipette all the supernatant into a 100 mL pear - shaped flask. Add the same volume of the mixed extraction agent to the residue and repeat the above ultrasonic and centrifugation operations. Combine the two supernatants to ensure complete dissolution of the target substances. For glass wool adsorption tubes, cut them into pieces and transfer them to a 25 mL colorimetric tube. Add 20 mL of a n - hexane - dichloromethane mixture (volume ratio 1:1), ultrasonically elute in a 35°C constant - temperature water bath for 30 min. After filtering the eluate through qualitative filter paper, combine it with the solution in the absorption flask. All the combined extracts are dehydrated through a glass chromatography column pre - filled with 5 g anhydrous sodium sulfate at a flow rate of 1 drop per second. After the liquid completely flows out, rinse the anhydrous sodium sulfate column with 5 mL of a n - hexane - dichloromethane mixture (volume ratio 1:1), and collect all the filtrate. The purification process uses a silica gel chromatography column. The column

is filled in sequence with 1 cm high - purity anhydrous sodium sulfate and 10 g activated silica gel. Pre - rinse the chromatography column with 20 mL n - hexane, discard the eluate, then transfer the dehydrated extract to the column, and elute with 50 mL n - hexane - dichloromethane mixture (volume ratio 3:1). Collect the eluate and evaporate it to about 0.5 mL by rotary evaporation, transfer it to a 1 mL volumetric flask, make up the volume to the mark with n - hexane, and filter through a 0.22μm organic - phase filter membrane for determination.

4) Chromatographic detection conditions. The GC inlet was operated in split/splitless mode, set at a temperature of 290°C, maintained in splitless mode for 0.8 min after injection, then switched to a split ratio of 10:1. Helium of 99.999% purity was used as the carrier gas, controlled in constant pressure mode with an initial column head pressure of 15 psi, automatically adjusted to 18 psi when the column temperature reached 200 °C, ensuring a stable linear carrier gas velocity of approximately 35 cm/s across different temperatures. The column temperature program was as follows: initial temperature set at 80°C, held for 2 min, ramped at 15°C/min to 180°C, then at 8°C/min to 260°C, and finally at 5°C/min to 300°C, held for 15 min. The mass spectrometer was operated with an electron ionization source, electron energy set at 70eV, ion source temperature maintained at 250°C, transfer line temperature at 300°C, and quadrupole temperature at 150°C. Argon of 99.99% purity was used as the collision gas, with the collision cell pressure maintained at 1.5 m Torr. The detection mode was multiple reaction monitoring (MRM), with characteristic ion pairs optimized for different brominated flame retardants; for example, m/z 486 → 406 and m/z488 → 408 were selected as the quantifier and qualifier ion pairs for BDE-28, with collision energies set at 16eV and 17eV, respectively; for TBBPA, m/z 543 → 463 and m/z545 → 465 were selected, both with collision energy of 22eV, and the dwell time for each ion pair was set at 50ms.

2.4 Data Processing

The raw data generated during the experiment was collected and integrated using a Thermo Xcalibur 4.1 workstation. For the quantitative analysis of brominated flame retardants, a standard curve was constructed based on the concentration gradient of the mixed standard working solution and the corresponding chromatographic peak areas. The linear regression equation was calculated by the least squares method, ensuring that the correlation coefficient (R^2) of the equation was not less than 0.995. The content of each target in the sample was calculated using the external standard method, that is, the specific concentration value [7] was obtained by comparing the peak area of the target in the sample solution with the standard curve. To ensure the reliability of the data, three parallel experiments were set for each electronic waste sample, and the final results were presented in the form of the average of the three measured values combined with the standard deviation. The method precision was evaluated by the relative standard deviation (RSD), and the calculation was based on the measured values of the three parallel experiments, requiring the RSD to be controlled within 10%. The method accuracy was verified by the spike recovery experiment. Standard solutions at three levels (10 ng/g, 50 ng/g, 100 ng/g) were added to the samples respectively. After pretreatment and detection, the percentage of the actual measured amount to the theoretical added amount was calculated. For the migration and transformation characteristics of brominated flame retardants during the pyrolysis process, the migration rate was calculated as the percentage of the total amount of the target in the gas-phase and liquid-phase products to the initial total content of the sample, and the conversion rate was calculated as the ratio of (initial total content - residual amount in the pyrolysis residue) to the initial total content, so as to quantify the migration efficiency and conversion degree of brominated flame retardants under different pyrolysis conditions.

3. RESULTS AND ANALYSIS

3.1 Influence of Pyrolysis Temperature on the Migration of Brominated Flame Retardants

At 300 °C, the total migration rate of brominated flame retardants is at a relatively low level of 15% - 25%. At this time, more than 80% of the migrated products exist in the form of liquid tar. This is because under low-temperature conditions, the intensity of molecular thermal motion is limited. Brominated flame retardants mainly achieve migration through their own volatilization, and the matrix of electronic waste has not undergone significant decomposition, with a strong wrapping effect on the flame retardants, restricting their diffusion into the gas phase [8]. When the temperature rises to 400 °C, the total migration rate increases to 35% - 50%, and the proportion of flame retardants in the liquid tar decreases to 60% - 70%, while the proportion of gaseous products begins to increase. When it reaches 500 °C, the total migration rate further increases to 60% < 75%, and the proportion of gaseous products increases significantly. Among them, the gaseous proportion of PBDEs reaches 35% - 45%, and the gaseous proportion of TBBPA reaches 20% - 30%. When the temperature rises to 600 °C, the total migration

rate exceeds 80%, and gaseous products become the main form of migration, with a proportion exceeding 50%. At 700 °C, the total migration rate reaches over 90%, and the proportion of gaseous products is as high as 60% - 70%. Different types of brominated flame retardants show obvious differences in migration rates. The migration rates of low-brominated PBDEs such as BDE-28 and BDE-47 are always higher than those of high-brominated PBDEs such as BDE-183.

3.2 Pyrolytic Transformation Pathways of Brominated Flame Retardants

Within the pyrolysis range of $300 \sim 600°C$, the debromination reaction of PBDEs shows significant temperature dependence. When the temperature rises to $400°C$, the $C-Br$ bond in the molecule of high-brominated homologues such as BDE-183 breaks first due to the enhanced thermal vibration energy, releasing bromide ions and generating low-brominated product BDE-153. As the temperature continues to rise to 500 °C, BDE-153 further undergoes debromination to form BDE-99. For TBBPA, the debromination reaction at the ortho-position of the phenolic hydroxyl group starts at around 450 °C, generating tribromobisphenol A. When the temperature exceeds $550°C$, the ether bond in the molecular backbone breaks, and the debromination products are further converted into bromophenol compounds, among which the production amount of 2, 4, 6-tribromophenol accounts for more than 60% of the total debromination products.

3.3 Influence of E-waste Materials on Migration and Transformation

The differences in the physicochemical properties of e-waste with different materials directly affect the migration and transformation behavior of brominated flame retardants during pyrolysis. The outer shell of waste TVs is mostly made of ABS material, and the pore structure generated by the premature decomposition of the matrix provides more migration channels for PBDEs molecules, making the migration rate of PBDEs reach $(72.3 \pm 3.5)\%$ at $500°C$, significantly higher than that of computer motherboards. The brominated epoxy resin in computer motherboards has a three-dimensional network structure and is tightly bound to TBBPA by covalent bonds. Higher energy is required to break the binding force during pyrolysis, resulting in a conversion rate of TBBPA of only (58.2±4.1) % at $500°C$, lower than that of the keyboard sample made of HIPS material. In addition, metal impurities such as copper and iron contained in computer motherboards have unpaired electrons on their surfaces that can adsorb bromine atoms in brominated flame retardant molecules, reducing the activation energy of the debromination reaction and making the production of low-brominated products (such as BDE-47) 15% - 20% higher than that of TV outer shells. The styrene units contained in the keyboard material will undergo an addition reaction with bromine radicals, inhibiting the debromination process to a certain extent.

4. CONCLUSION

Through systematic experiments, the migration and transformation rules of brominated flame retardants during the pyrolysis of electronic waste were explored. It was found that the pyrolysis temperature and material type had significant effects on their behavior: with the increase in temperature, the migration rate increased significantly and the proportion of gaseous products increased, and the debromination reaction was the main transformation path; PBDEs were more likely to migrate in ABS materials, the brominated epoxy resin matrix inhibited the transformation of TBBPA, and metal impurities promoted debromination. The research results can not only provide direct data support for optimizing the pyrolysis process parameters of electronic waste, but also provide a theoretical basis for the subsequent development of pollution control of brominated flame retardants during the pyrolysis process. Future research can further explore the effects of different pyrolysis atmospheres and catalyst addition on the migration and transformation of brominated flame retardants, and provide more comprehensive technical support for the green and efficient pyrolysis treatment of electronic waste.

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