Rapid determination of certain BFRs in plastics by X-ray fluorescence spectrometry (XRF) and thermal desorption GC-MS (TD-GC-MS) for the RoHS directive

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Abstract

A fast analytical method was designed to quantify certain brominated flame retardants (BFRs) in plastic materials by the combination of X-ray fluorescence spectrometry analysis (XRF analysis) and a thermal desorption gas chromatographical analysis with mass spectrometry (TD-GC-MS). There was focus on the characterisation of polybrominated diphenyl ethers (PBDEs) in polystyrene, polycarbonate and polymethylmethacrylate to check the fulfilment of the RoHS directive. Recoveries for PBDEs from 69 to 112 % have been reached. Other brominated flame retardants have been used to simulate RoHS negative samples. The main advantage of this method is its quickness and minimum sample pre-treatment.

Introduction

For a long time brominated flame retardants (BFRs) have been widely used in all kind of materials belonging to electric and electronic equipment, furniture, building products, etc. The widespread of BFRs in public places, housing, offices, airplanes and vehicles results in a higher fire safety. The disadvantage is an overall pollution by BFRs and their undesirable by-products in the environment.[1] A part of the plastic waste stream from electric and electronic equipment (WEEE) might contain polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs). To prevent further re-use and production of WEEE containing PBDEs and PBBs the European Union published on 13th February 2003 a new regulation. This contains a restriction of hazardous substances (RoHS) like lead, mercury, cadmium, chromium (VI), PBBs and PBDEs. The RoHS became a law since July 2006. The content of these chemicals/elements in new electric and electronic equipment shall not exceed a limit of 1000 mg/kg.[2]

Various methods for the quantification of BFRs in plastics are based on a solvent extraction followed by GC-MS or LC-MS analysis. This is time consuming and the recovery is depending on each type of plastic. The necessity to invent a quick method comes from the industry itself as their quality control departments would like to test each batch of polymers after delivery. The method described in this paper is a first step to develop an analytical method to quantify BFRs in different polymers by a fast and universal method. This can be done by a combination of X-ray fluorescence spectrometry analysis (XRF analysis) for the quantification of total bromine and a thermal desorption gas chromatography analysis with mass spectrometry (TD-GC-MS) for the identification of BFRs.

Materials and Methods

Chemicals

All PBDE solutions used in this study are made from technical mixtures of pentaBDE and decaBDE in toluene (HPLC grade). Tetrabromobisphenol A (TBBP A) and a calibration PBDE mix of individual congeners were synthesised by AccuStandard (New Haven, CT, USA). Hexabromocyclododecane (HBCD) was a technical grade. Calibration solutions for XRF analysis were made of tetrabromomethane in toluene. The polymer solutions were made with HPLC grade solvents.

XRF method

The XRF analysis was performed with an Oxford Instruments ED 2000 Ag spectrometer under the conditions for measuring of medium elements in air, tube voltage of 45 kV, the current to the tube was 50 mA with a time of measuring of 30 seconds. The intensity of Br K_α was automatically corrected for potential overlapping lines of

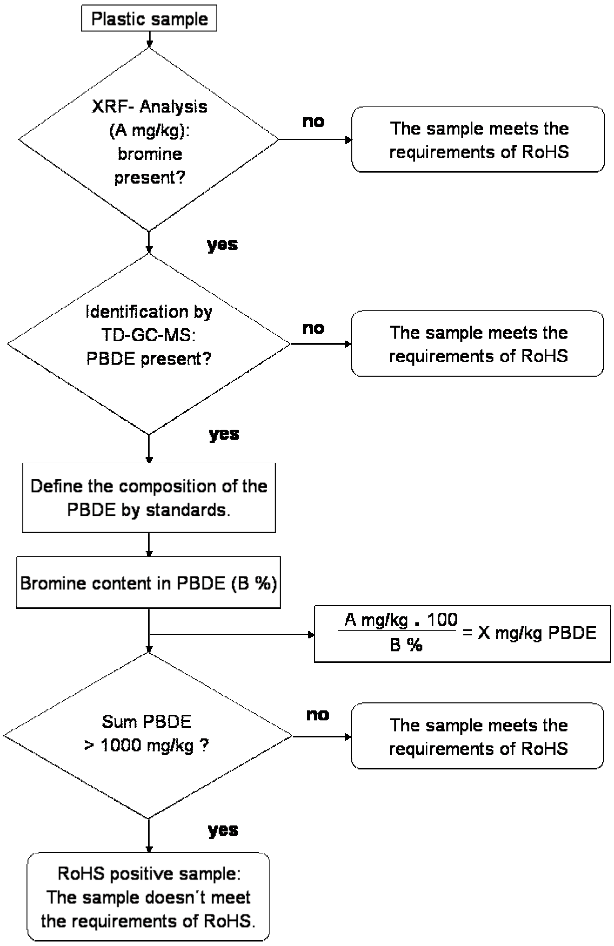
As, Hg and Ru. The calibration for bromine was done in a range from 0,02 to 6 w/w % with the application of "Self absorption" regression model.

TD-GC-MS method

All experiments were carried out with a thermal desorption and pyrolysis unit PY-2020iD (Frontier Laboratories Ltd., Japan) with a 48 position auto-sampler connected to a GC-MS-QP2010plus (Shimadzu, Japan). DecaBDE is a thermal labile product and requires a short residence time on the analytical column. Therefore a special metal capillary separation column (Ultra ALLOY-PBDE; 0,25 mm i.d. x 15 m, Frontier Laboratories Ltd., Japan) coated with a very thin (0,05 um) film of immobilized-polydimethylsiloxane is used. After optimising of desorption settings thermal desorption temperature of 330°C for 5 minutes gave the highest and the most stable peak performance of decaBDE. The pyrolysis interface and the GC injector were kept at 320°C. The m/z scan was in a range from 150 to 1000.

The combination of the XRF-analysis and TD-GC-MS results

The XRF analysis measures the bromine content in the samples. In case there is no bromine presented the sample will pass the RoHS limits. The limit of detection (LOD) of XRF for bromine is approx. 10 mg/kg in hydrocarbon matrix. If there is bromine presented in the sample a TD-GC-MS analysis has to be done to identify the type of brominated compounds in the sample (Figure 1).



* The limit of detection for XRF analysis of bromine in hydrocarbon matrix is approx. 10 mg/kg

** The limit of detection for each PBDE by TD-GC-MS is approx. 50 mg/kg

Figure 1: Overview of the combined method for RoHS in the case of PBDE

By TD-GC-MS analysis of a calibration PBDE mix of individual congeners response factors for each homologous can be obtained. When analysing real samples with the technical mixtures of PBDE, the bromine content in any technical PBDE mixture can be calculated. With the combination of the total bromine content in the sample, obtained by XRF method and the bromine content in used technical PBDE mixture, obtained by TD-GC-MS a total content of PBDEs in the sample can be calculated. If the concentration of sum of PBDE congeners in the sample is higher than 1000 mg/kg the sample will not pass the limits according to RoHS.

Experimental design

The performance of the method has been shown by the analysis of different concentrations of chosen PBDEs, tetrabromobisphenol A (TBBP A) and hexabromocyclododecane (HBCD) in different kind of polymers (polystyrene, polycarbonate and polymethylmethacrylate). At the moment of this study a technical mixture of PBBs was not available, so this experiment is mainly focussing on PBDEs. The samples were made by fusion of a polymer solution and a BFR standard solution. After evaporation of the solvent a BFR doped plastic specimen remains. The polymers are fast solving in solvents like toluene (polystyrene), acetone (polymethylmethacrylate) and dichloromethane (polycarbonate), sample No. 4 has been blended also with antimony trioxide (Sb_2O_3). Polybrominated compounds and Sb_2O_3 are synergistic flame retardant compounds. They are frequently used in polystyrene. The influence of Sb_2O_3 on the XRF measurement should be examined.[3]

Sample preparation

The sample preparation for a XRF analysis requires cutting the samples in a size they fit in the XRF sample cup. The samples should have the thickness more than critical one.

The TD-GC-MS analysis requires a very small piece of sample (5-0,1 mg) to be cut and put into a stainless steel sample cup. This sample cup is placed into an auto-sampler and during thermal desorption heated in the furnace of the pyrolyzer.

Results and Discussion

The results shown in Table 1 give a combination of the measurement on XRF and TD-GC-MS for the spiked samples. According to XRF analysis all samples were positive for bromine and TD-GC-MS identified all the brominated compounds. The bromine content in the PBDE technical mixtures was determined by comparison with a PBDE calibration mixture of individual congeners. The bromine content in HBCD and TBBP A was calculated from the molecular weight. The polystyrene samples give a good recovery for BFRs between 69 and 93 % except for sample 3 (TBBP A) with the recovery of 51 %. The presence of Sb_2O_3 in polystyrene (sample 4) did not influence the result from the XRF analysis and the sample had a comparable recovery like the sample without Sb_2O_3 (sample 5). The recovery of BFRs in polymethylmethacrylate and polycarbonate was between 80 and 115 %.

Regarding the expected uncertainty of the whole measurement it will be necessary to set a safety interval (possibly 700-1000 mg/kg of PBDE) in which the samples will be considered as a potential RoHS positive and the exact concentration should be determined by a different analytical method.

Table 1: Results of analysis of BFR spiked samples and their recovery.

Sample number	Matrix	Identified BFR compound	Measured bromine content (mg Br/kg)	BFR bromine content (% Br)	Calculated BFR content (mg BFR/kg)	Theoretical BFR content (mg BFR/kg)	Recovery (%)
1	Polystyrene	HBCD	659	75,4	874	943	93
2	Polystyrene	HBCD	1229	75,4	1630	1815	90
3	Polystyrene	TBBP A	608	58,8	1034	2046	51
4*	Polystyrene	pentaBDE	1551	70,4	2203	2500	88
5	Polystyrene	pentaBDE	2071	70,4	2942	3874	76
6	Polystyrene	decaBDE	608	70,4	732	1043	70
7	Polystyrene	decaBDE	2066	83,0	2489	3139	79
8	Polystyrene	decaBDE	2902	83,0	3496	5050	69
9	Polymethylmethacrylate	HBCD	648	75,4	860	979	88
10	Polymethylmethacrylate	HBCD	1268	75,4	1682	1944	87
11	Polymethylmethacrylate	pentaBDE	1461	70,4	2076	2347	89
12	Polymethylmethacrylate	decaBDE	730	83,0	880	1064	83
13	Polymethylmethacrylate	decaBDE	1633	83,0	1697	1762	112
14	Polycarbonate	HBCD	653	75,4	865	885	98
15	Polycarbonate	HBCD	1409	75,4	1870	1622	115
16	Polycarbonate	pentaBDE	2106	70,4	2992	3726	80
17	Polycarbonate	decaBDE	694	83,0	836	1019	82
18	Polycarbonate	decaBDE	1512	83,0	1822	2196	83

* Sample 4 contains Sb_2O_3 (33 w/w %)

The method of TD-GC-MS with the combination of XRF measurement seems to be a good quick tool for processing control of polymers according to the RoHS requirements. The TD-GC-MS gives to the laboratory not only a control of fulfilment of RoHS directive, but also control of the whole polymer composition/additive presence.

Further investigation will be done on the direct quantification of PBDEs in different plastic materials with TD-GC-MS. Pathways as standard addition and external calibration with internal standards will be checked. Other BFRs like the PBBs and not RoHS described BFRs should be possible quantified. A further step has to be done with the other BRFs like HBCD, TBBA in a combination with RoHS banned flame retardants.

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