OPTIMISATION OF A MS/MS METHOD FOR DBDPE: APPLICATION TO SPANISH SEWAGE SLUDGES

De la Torre A, Concejero MA, Sanz P, Martinez MA

Persistent Organic Pollutant Group, Environment Department. CIEMAT, Avd. Complutense 22 Madrid, Spain.

Abstract

In this study, fourteen sewage sludges from different Spanish Wastewater Treatment Plants (WWTPs) were analysed for Decabromodiphenyl ethane and Decabromodiphenyl ether. The presence of a "new" brominated flame retardant, DBDPE, has been confirmed. Decabromodiphenyl ethane was positively identified and quantified by MS/MS in all the samples analysed with levels ranging from 14 to 90 ng/g dry weight. The concentrations are low compared to DecaBDE, which probably reflects the higher usage of DecaBDE.

Introduction

The brominated flame retardant decabromodiphenyl ethane, DBDPE, is marketed as an alternative to decabromodiphenyl ether, DecaBDE[1] (see Figure 1). Decabromodiphenyl ethane is a relatively new BFR with similar applications to that of DecaBDE (i.e. as an additive flame retardant in different types of plastic and textiles). It was introduced in the early 1990s under a trade name SAYTEX® 8010 by Albermarle Corporation[2]. Although its not as widely used as DecaBDE due to their higher cost, it is predicted that their use will increased considerably [3]. In Europe, it is commercialized as a BFR that meets the German Dioxin Ordenances [4,2]. In contrast to DecaBDE its produces no polybrominated p-dioxins and only minor quantities of 2,3,7,8-tetrabromodibenzo-p-furan under pyrolysis conditions [4,5].

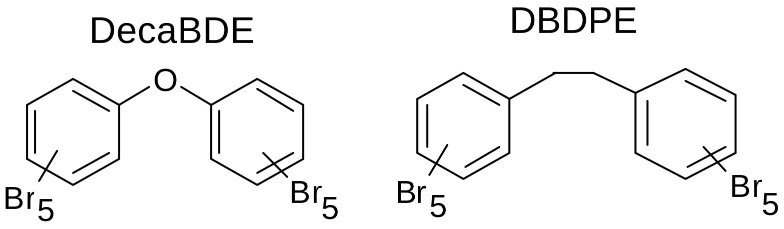


Figure 1. Chemical structures of DecaBDE and DBDPE.

This study has two objectives: the development of a MS/MS method to analysed DBDPE and its application to sewage sludge samples from Wastewater Treatment Plants (WWTPs) from Spain.

Materials and Methods

Sample collection:

Sewage sludges were sampled from fourteen Wastewater Treatment Plants (WWTPs) of different sizes and geographic distributed all over Spain. Samples were dried at 40°C until constant weight to avoid lack of volatile congeners and poured into sealed amber-glass flasks for preserving from light, humidity and other external factors which might changes its chemical composition. Upon receiving in the laboratory, they were ground to a fine powder, reducing as much as possible the time between collection and analysis.

According to the type of influent stream and number of inhabitants, the different facilities were divided into several categories shown in Table 1. "Urban" refers to waste-water from highly-populated/low-industrialised sites; "Industrial", to zones with high industrial activity cores and "Mixture", to mixed urban and industrial activities.

Table 1. Type of influent and number of inhabitants related to each facility evaluated.

Category	Type of Influent	Number of inhabitants
U1	Urban	Lowly populated (< 500.000)
U2	Urban	Medium populated (500.000 – 1.000.000)
U3	Urban	Highly populated (> 1.000.000)
M1	Mixture	Low populated (< 500.000)
M2	Mixture	Medium populated (500.000 – 1.000.000)
I1	Industrial	Low populated (< 500.000)
I2	Industrial	Highly populated (< 500.000)

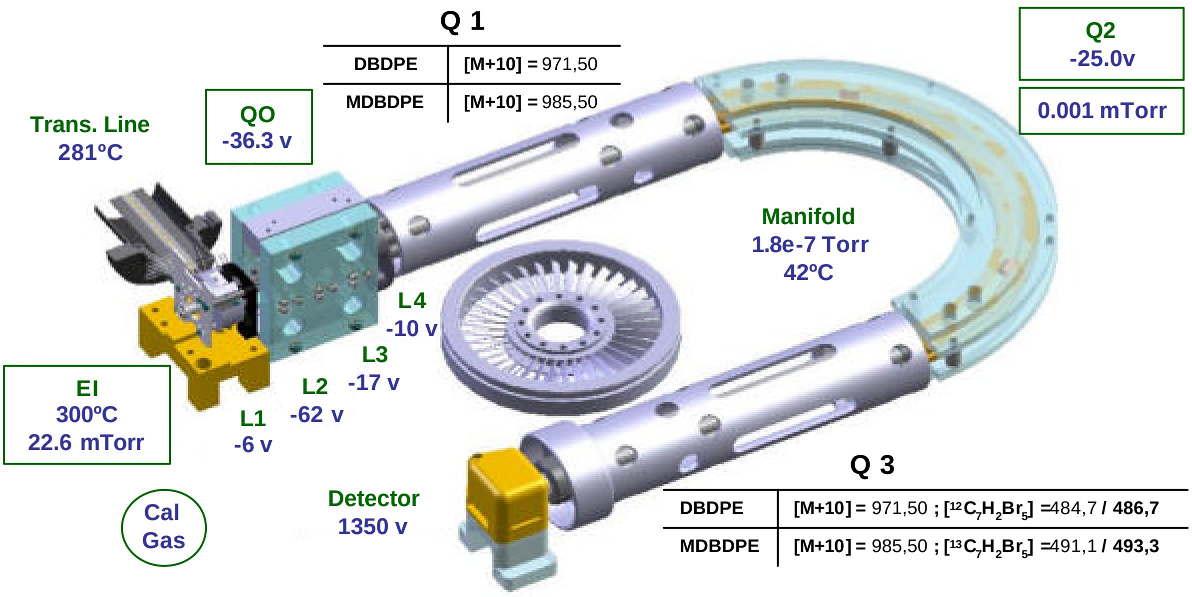
Sample Extraction and Clean up:

An amount of 0.5 g of dried sewage sludge was spiked with a known amount of MDBDPE and MDBDE standard solutions (Wellington Laboratories Inc., Canada) and then extracted with a mixture of hexane:dicloromethane (1:1) 100ºC, 1500psi, 90% volume and three static cycles, using an ASE 100 system (Accelerated Solvent Extraction). Resulting extracts were transferred into a separation funnel and liquid-extracted with concentrated sulphuric acid to remove organic matter. Clean-up stage was then performed in an automated purification Power PrepTM System (FMS, Inc., USA) including acidic silica gel and basic alumina columns. Different mixtures of hexane:dicloromethane were used to recover target analytes while retaining interfering compounds. The extracts obtained were concentrated and further analysed by GC-MS.

Sample Analysis:

Analyses of **DecaBDE** were carried out by GC-NCI-MS in a Agilent 6890 Gas Chromatograph equipped with a 7683 Autosampler, and a temperature programmable injector (PTV) working in pulsed splitless. The GC was connected to a Low Resolution Mass Spectrometer (LRMS) detector, Agilent 5973 MSD Network. Ammonia was used as the chemical ionisation moderating gas at 2.1 x 10^{-4} Torr ion source pressure. For DBDPE and DecaBDE a J&W Scientific DB-5MS (15 m x 0.25 mm x 0.10 µm film thickness) capillary column was used for its determination, with helium as the carrying gas, working with the same temperature program, from 140ºC (held for 1 min.) to 310 ºC (held for 7.5 min.) at 20ºC/min, using pulsed splitless injection mode (30psi pulsed pressure). Injector temperature was 280 ºC (held 15 min).
Identification and quantification of DecaBDE was carried out using isotopic dilution, monitoring masses m/z 484.7 and 486.7 ($^{12}C_6Br_5O^-$) and m/z 494.7 and 496.7 ($^{13}C_6Br_5O^-$) [6,7].

On the other hand, analysis of **DBDPE** was carried out by GC/MS/MS in a Varian 320-MS-TQ Spectrometer equipped with a CP-3800 Gas Chromatograph and a Varian CP-8400 Autosampler. The election of the masses to monitoring was developed in order to avoid the overlap of the base peak related to the loss of 6 bromines of DBDPE (fragment $^{12}C_{14}H_4Br_4$) and the pentabromobenzyl fragment (^{13}C7H2Br5) of MDBDPE, as described by Konstantinov et al [8]. In this case, the MS/MS feasibility allowed to solve this problem. First of all, the molecular ions (M+10) of DBDPE and MDBDPE were isolated in the first quadrupole. Then, after optimizing the collision voltages in the second quadrupole, the masses m/z 486.6/484.7 ($^{12}C_7H_2Br_5^+$) + m/z 971.4 ($^{12}M+10^+$) for DBDPE and m/z 493.3/491.1 ($^{13}C_7H_2Br_5^+$) + m/z 985.5 ($^{13}M+10^+$) for MDBDPE were monitored in the third quadrupole (see Figure 2). So finally, masses m/z 486.6 for DBDPE and m/z 493.3 for MDBDPE were used to quantified, and masses m/z 484.7 / 971.4 for DBDPE and m/z 491.1 / 985.5 for MDBDPE as qualifiers. To conclude the optimization, some probes with different electron energies, 70ev and 20ev were performed, (see Figure 3). As expected, better S/N ratio was found with 20ev. The low energy produced less fragmentation of the molecular ion in the first quadrupole and, consequently, more sensibility was achieved in the second ionization in Q2, which means lastly, better LODs in the final quantification.



DBDPE	**[M+10] =** 971,50
MDBDPE	**[M+10] =** 985,50

DBDPE	**[M+10] =** 971,50 **;** $[^{12}C_7H_2Br_5]$ = 484,7 **/ 486,7**
MDBDPE	**[M+10] =** 985,50 **;** $[^{13}C_7H_2Br_5]$ = 491,1 **/ 493,3**

Figure 2. Operational conditions and masses monitored: targets ions (bold) and qualifiers ions (normal)

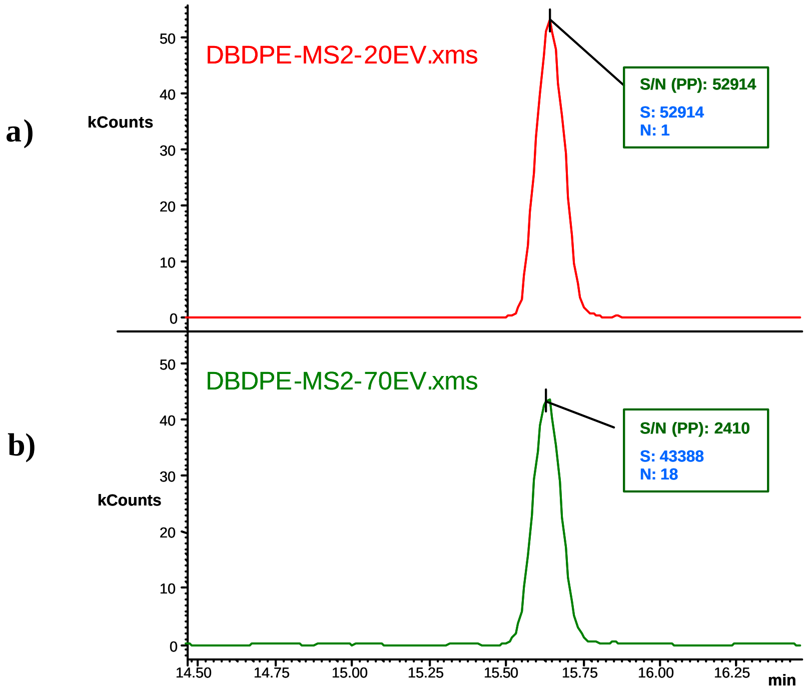


Figure 3. Chromatograms obtained in MS^2 with **a)** 20e.v. and **b)** 70e.v. for DBDPE.

With the optimised GC-MS and GC-MS/MS conditions, 5 point calibrations were used for DBDPE and DecaBDE to determine their concentration in the sludge samples. Good linearity was observed in both cases. Correlation coefficients were 0.998 for DBDPE and 0.993 for DecaBDE. Limits of detection, LODs, were defined as the smaller concentration giving a signal with S/N>3. LODs obtained for DBDPE ranged from 0.007 to 0.045 ng/g d.w. while for DecaBDE ranged from 0.1 to 0.2 ng/g d.w.

Results and Discussion

Concentration levels of the sludges analysed are listed in Table 2.
Decabromodiphenyl ethane was detected in all samples from 14 to 90 ng/g d.w., whereas DecaBDE was found at higher levels, ranging from 76 to 1136 ng/g d.w. Concentrations obtained in this study for DecaBDE are similar to those reported previously in Spain [9]. As the same time, DBDPE content is in the same level than those described for Swedish sludges (from not detected up to 100 ng/g d.w.)[1] and higher than those found in Canada (from 6 to 32 ng/g d.w.)[8]. Taking into account the wide data variation, it could not be found evidences of the influence of the different WWTP conditions, such as the type of influent entering the plant and/or the number of inhabitants related to that area. Although important differences could be established between urban and mixture or industrial areas for DecaBDE, no significant variations could be observed for DBDPE.

Decabromodiphenyl ethane/DecaBDE ratio was calculated, obtaining values from 0.03 to 0.6. Similar data were reported in Sweden sludges (from 0.02 to 0.7)[1]. The high variability of this ratio seems to indicate that the products are used independently.

Table 2. DBDPE and DecaBDE concentrations of Spanish sewage sludges in ng/g d.w.

Sample	DBDPE (ng/g d.w.)	DecaBDE (ng/g d.w.)	Ratio DBDPE/DecaBDE
U1-1	39,85	364,100	0,109
U1-2	27,07	86,990	0,311
U2-3	22,254	714,910	0,031
U2-4	19,753	224,470	0,088
U3-5	32,069	114,180	0,281
U3-6	41,158	426,300	0,097
M1-7	21,565	103,440	0,208
M1-8	43,666	76,190	0,573
M2-9	14,935	121,740	0,123
M2-10	72,454	207,300	0,350
I1-11	32,262	345,650	0,093
I1-12	90,054	1136,210	0,079
I2-13	24,073	451,920	0,053
I2-14	21,136	185,000	0,114

References

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