

## NCI-MS vs EI-MS for PBDEs analysis in Spanish sewage sludges

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### Introduction

Polibrominated diphenyl ethers are emerging contaminants whose persistence, potential bioaccumulation and toxic risk to humans and wildlife cause large concern (WHO 1197, 1997). Nowadays, the knowledge of these compounds, their occurrence, behaviour, and their fate in the environment is quite limited. However, analytical methods for PBDEs determination have undergone rapid development in the last five years, mainly being based on established methods for chlorinated pollutants (Eljarrat, E, 2004). At the same time several international interlaboratory exercises have been organized. In the first world-wide interlaboratory study organised between 1999 and 2000, results for BDE 47 were acceptable, but those for BDE 99, 100, 153 and 154 showed that a further improvement of these analysis was needed (de, Boer J., 2002). That study also showed that BDE 209 analysis was not under control. Nevertheless, due to laboratories have modified their methodology the results have improved (Takahashi, S., 2006).

The current study is focused on the separation and quantification of PBDEs, including decaBDE, by high resolution gas chromatography in combination with mass spectrometry working in electron impact (EI) or negative chemical ionization (NCI) modes. For evaluating and comparing both techniques different Spanish sewage sludge samples were analyzed.

### Materials and Methods

The isomeric separation was carried out by an 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. A J&W Scientific DB-5MS (15 m x 0.25 mm x 0.10  $\mu\text{m}$  film thickness) capillary column was used for its determination, with helium as the carrying gas at a constant pressure of 10 psi. The temperature program was from 140°C (hold for 1 min.) to 310 °C (hold for 5 min.) at 20°C/min. Injector temperature was from 270 °C (hold for 0.5 min) to 300°C (hold for 15.5 min.) at 720°C/min. The GC method was developed in order to avoid thermal degradation of decaBDE, using short and narrow GC columns with thin films, moderated injector and column temperatures, and short injection residence times (de, Boer J., 2006). The chromatographic method allows 21 PBDEs separation including deca-209-BDE. A typical chromatogram can be seen in Figure 1 (left).

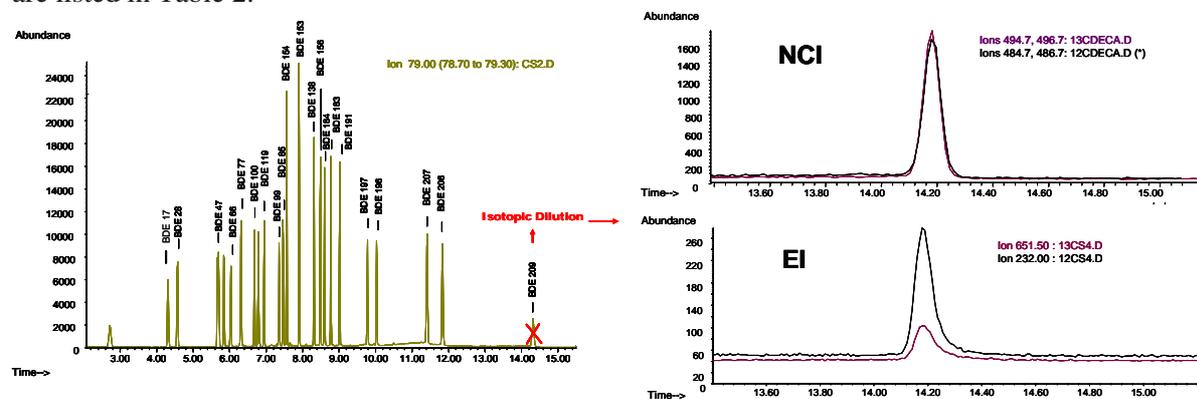
All the congeners were analysed by GC-NCI-MS and GC-EI-MS. For NCI analysis ammonia was used as the chemical ionisation moderating gas at  $2.1 \times 10^{-4}$  Torr ion source pressure. Other operation conditions were 250°C ion source temperature, 150°C quadrupole temperature and 320°C transfer line temperature. For EI analysis, the operation conditions were 230°C ion source temperature, 150°C quadrupole temperature and 280°C transfer line temperature.

The settings of both different techniques are shown in Table 1. The main NCI drawback is that most PBDE isomers can be only monitored with bromine ions,  $m/z$  79 ( $^{79}\text{Br}$ ) and  $m/z$  81 ( $^{81}\text{Br}$ ) (de, Boer J., 2001). In this case the identification and quantification was carried out using the BDE-MXE solution (Wellington Laboratories, Ontario, Canada) as external standard. Some preliminary tests, using isotopic dilution for quantifying decaBDE have started, monitoring masses  $m/z$  484.7 and 486.7 ( $^{12}\text{C}_6\text{Br}_5\text{O}$ ) and  $m/z$  494.7 and 496.7 ( $^{13}\text{C}_6\text{Br}_5\text{O}$ ) as reported by Björklund et al. 2003 (Björklund, J., 2003), and results and conclusions will be presented during the Workshop. On the other hand, when working in EI mode, identification and quantification of target species were carried out by following

criteria of isotopic dilution, for allowing high accuracy in the calculation of the final results. In this case the three most abundant isotope peaks were monitored for each level of bromination, corresponding to molecular cluster for tri-BDEs ( BDE 17 and 28) and tetra-BDE 77, and  $[M-2Br]^+$  for tetra to nona-BDEs (BDE 47, 66, 100, 119, 99, 85, 154, 153, 138, 156, 184, 183, 191, 197, 196, 207, and 206). For  $^{12}C$ -BDE 209 the most abundant isotope peaks corresponded to the molecular cluster ( $C_6Br_2$ ) but due to the high complexity of the matrixes analysed (sewages sludges) some problems have been found with this cluster for  $^{13}C$  so, consequently, the four bromines loss mass spectra  $[M-4Br]^+$  were monitored, see Table 1. The analysis in EI mode was performed using a BDE-CVS-E calibration solution from Wellington Laboratories (Ontario, Canada).

## Results and Discussion

Calibration curves were obtained for the 21 polybrominated diphenyl ethers, both in EI and NCI mode, in the range of 1- 400 pg/ $\mu$ l for tri to penta-BDE, 2-800 pg/ $\mu$ l for hexa to octa-BDE and 5-800 pg/ $\mu$ l for nona and deca-BDE. Good linearity was observed in all the cases. Correlation coefficient values are listed in Table 2.



**Figure 1.-** Left: NCI-MS chromatogram. Right: decaBDE peaks when isotopic dilution is used.

The method developed was applied to four sewage sludge samples from Spanish municipal waste water treatment plants. Concentration levels are listed in Table 2. Results obtained with both techniques were similar but some deviation has been found. Concretely, decaBDE levels related to EI were higher than those obtained by NCI. This deviation could be due to the quantification by external standard. In order to evaluate such effect and enhance data quality, some preliminary tests with standards have been already done by using isotopic dilution in NCI mode for decaBDE, Figure 1 (right). A significant improvement of decaBDE signal can be observed. Environmental data will be shown during Workshop.

Limits of Detection LODs, defined as the smaller concentration giving  $S/N = 3$ , are listed in table 1. The lowest LODs were obtained with the GC-NCI-MS, increasing with the bromination degree. They were lower than those obtained by EI: approximately 2-3 times for tri to hexa-BDEs, 3-10 times for hexa to nona-BDEs and 3 times for deca-BDE. LODs show that NCI mode is more sensitive, but less selective than EI mode, because does not give structural information and characterization of the bromination degree. However, EI mode allows to use isotopic dilution for all the congeners.

Taking into account that deca isomer contribution is the most relevant in environmental samples as the sewage sludges studied, further works using isotopic dilution in NCI mode are needed to improve the quality of measurements.

**Table 1.-** Selected ions for the GC-EI-MS and GC-NCI-MS: targets ions (bold) and qualifiers ions (normal letter).

	Ions Monitored				
	Compound	R.T. (min)	GC-EI-MS		GC-NCI-MS
TriBDEs	<b>28L</b>	4.53	<b>418,420,422</b>	<b>[M+2]<sup>+</sup>, [M+6]<sup>+</sup>, [M+8]<sup>+</sup></b>	
	<b>17</b>	4.26	<b>406,408,401</b>	<b>[M+2]<sup>+</sup>, [M+6]<sup>+</sup>, [M+8]<sup>+</sup></b>	79, 81
	<b>28</b>	4.53			
TetraBDEs	<b>47L</b>	5.80	<b>336,338,340</b>	<b>[M-2Br]<sup>+</sup>, [M-2Br+2]<sup>+</sup>, [M-2Br+4]<sup>+</sup></b>	
	<b>47</b>	5.80	<b>324,326,328</b>	<b>[M-2Br]<sup>+</sup>, [M-2Br+2]<sup>+</sup>, [M-2Br+4]<sup>+</sup></b>	79, 81
	<b>66</b>	5.99			
	<b>77</b>	6.30			
PentaBDEs	<b>99L</b>	6.90	<b>416,418,420</b>	<b>[M-2Br+2]<sup>+</sup>, [M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup></b>	
	<b>100</b>	6.63	<b>404,406,408</b>	<b>[M-2Br+2]<sup>+</sup>, [M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup></b>	79, 81
	<b>119</b>	6.75			
	<b>99</b>	6.90			
	<b>85</b>	7.30			
HexaBDE	<b>154L</b>	7.51	494, <b>496</b> ,498	<b>[M-2Br+2]<sup>+</sup>, [M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup></b>	
	<b>153L</b>	7.86			
	<b>138L</b>	8.26			
	<b>154</b>	7.51	482, <b>484</b> ,486	<b>[M-2Br+2]<sup>+</sup>, [M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup></b>	79, 81
	<b>153</b>	7.86			
	<b>138</b>	7.26			
<b>156</b>	8.44				
HeptaBDEs	<b>183L</b>	8.73	<b>574,576,578</b>	<b>[M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup>, [M-2Br+8]<sup>+</sup></b>	
	<b>184</b>	8.56	<b>562,564,566</b>	<b>[M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup>, [M-2Br+8]<sup>+</sup></b>	79, 81
	<b>183</b>	8.73			
	<b>191</b>	8.98			
OctaBDEs	<b>197L</b>	9.74	652, <b>654</b> ,656	<b>[M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup>, [M-2Br+8]<sup>+</sup></b>	
	<b>197</b>	9.74	640, <b>642</b> ,644	<b>[M-2Br+4]<sup>+</sup>, [M-2Br+6]<sup>+</sup>, [M-2Br+8]<sup>+</sup></b>	79, 81
	<b>196</b>	9.98			
NonaBDEs	<b>207L</b>	11.34	<b>732,734,736</b>	<b>[M-2Br+6]<sup>+</sup>, [M-2Br+8]<sup>+</sup>, [M-2Br+10]<sup>+</sup></b>	
	<b>207</b>	11.34	<b>720,722,724</b>	<b>[M-2Br+6]<sup>+</sup>, [M-2Br+8]<sup>+</sup>, [M-2Br+10]<sup>+</sup></b>	79, 81
	<b>206</b>	11.76			
DecaBDE	<b>209L</b>	14.20	649.5, <b>651.5</b> ,653.5	<b>[M-4Br+6]<sup>+</sup>, [M-4Br+8]<sup>+</sup>, [M-4Br+10]<sup>+</sup></b>	
	<b>209</b>	14.20	230, <b>232</b> ,234	<b>M=<sup>12</sup>C<sub>6</sub>Br<sub>2</sub> [M]<sup>+</sup>, [M+2]<sup>+</sup>, [M+4]<sup>+</sup></b>	79, 81

**Table 2.-** Correlation coefficients of the calibration curves and LODs of all the congeners analysed in the Spanish sewage sludges. Concentrations in ng/g dw.

Congener	R <sup>2</sup>		LODs ng/g		Sample 1		Sample 2		Sample 3		Sample 4	
	EI	NCI	EI	NCI	NCI	EI	NCI	EI	NCI	EI	NCI	EI
17	0.9999	0.98	0,026	0.010	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.08
28	0.9999	0.99	0,030	0,010	0,08	0,08	0,03	N.D.	0,03	N.D.	0,21	0,20
47	0.9999	0.996	0,030	0,020	4,53	4,62	6,04	5,23	0,47	1,28	8,33	7,49
66	0.9999	0.994	0,049	0,020	0,11	N.D.	0,12	N.D.	0,05	N.D.	0,29	N.D.
77	0.998	0.99	0,036	0,011	N.D.	N.D.	N.D.	3,14	0,04	N.D.	0,24	N.D.
100	0.998	0.99	0,106	0,044	0,57	0,73	0,61	0,65	0,13	0,28	1,04	0,66
119	0.9996	0.98	0,791	0,041	0,13	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
99	0.9999	0.995	0,077	0,029	6,12	6,29	9,88	9,88	0,81	1,65	10,82	9,89
85	0.998	0.997	0,075	0,024	0,35	N.D.	0,61	0,44	0,11	N.D.	1,21	0,47
154	0.9998	0.998	0,068	0,028	0,41	0,19	0,54	0,18	0,28	0,12	1,51	0,25
153	0.999	0.998	0,050	0,056	1,30	0,82	2,13	1,25	0,45	0,34	2,97	1,19
138	0.999	0.997	0,375	0,034	0,49	N.D.	0,59	0,13	0,29	N.D.	1,55	1,37
156	0.996	0.998	0,556	0,036	0,30	N.D.	0,30	N.D.	0,20	N.D.	0,95	N.D.
184	0.997	0.998	0,221	0,059	0,38	N.D.	0,40	N.D.	0,30	N.D.	1,28	N.D.
183	0.998	0.997	0,111	0,066	1,13	0,89	1,29	0,91	0,28	0,68	2,18	1,81
191	0.996	0.988	0,084	0,024	0,28	N.D.	0,28	N.D.	0,20	N.D.	0,84	N.D.
197	0.999	0.993	0,219	0,015	0,76	N.D.	0,76	N.D.	0,29	N.D.	1,18	1,04
196	0.999	0.991	0,233	0,014	0,77	N.D.	0,60	N.D.	0,35	N.D.	1,10	0,93
207	0.998	0.999	0,622	0,092	3,00	3,06	3,64	2,36	3,44	2,63	4,17	3,98
206	0.996	0.998	1,028	0,093	3,96	2,34	4,09	3,50	3,31	3,30	4,81	4,28
209	0.996	0.993	1,564	0,557	98,41	92,59	75,16	88,70	110,76	144,96	105,26	124,62

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