Improvement of the GC/ECNI-MS response factors of compounds of technical toxaphene (CTTs) by pressure pulse splitless injection

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Abstract

Pressure pulse splitless injection improved the response factors of compounds of technical toxaphene (CTTs) up to factor 4 compared with concentional splitless injection. The pressure pulse during injection did not increase decomposition of the CTTs. The method can easily be added to standard quantitation methods without any disadvantage.

1. Introduction

The most widespread quantitation techniques for CTTs in environmental samples are GC/ECD and GC/ECNI-MS in the selected ion monitoring (SIM) mode. Unfortunately, the more selective GC/ECNI-MS technique exhibits strongly varying response factors for CTT congeners[1-3]. In addition, Alawi et al. found significantly lower CTT response factors after splitless injection than after on-column injection[4]. In the splitless mode, pressure pulse injection (PPI) was applied to particularly improve the response factors of CTTs with low vapor pressure such as B9-1025 (Parlar #62). PPI or electronic pressure programming injection was recently introduced[5] and already applied to improve the response factors of chlorinated hydrocarbons such as DDT, endrin[6], and CTTs[7-8]. Starting point of the present study was the GC/ECNI-MS method for the congener specific quantitation of CTTs which was recently published[1,8-9].

2. Experimental methods

GC/ECNI-MS parameters.
All measurements were performed on an HP 5989B MS Engine connected to an HP 5890 II plus gas chromatograph (Hewlett-Packard). The carrier gas was helium and the CI reagent gas was methane (both 5.0 quality, Linde, Germany). The optimized ion source pressure was 1.6 mbar. The GC/MS was manually tuned using m/z 302, m/z 414, and m/z 464 of PFTBA. The ion source and quadrupole temperatures were 150°C and 100°C, respectively. In the SIM mode we monitored m/z 340.9 and 342.9 for heptachloro CTTs, m/z 376.9 and 378.9 for octachloro CTTs, and m/z 410.8 and 412.8 for nonachloro CTTs. Dwell time was 50 ms each (2.53 cycles/sec). For quantitative measurements in biological samples, time windows (after a solvent delay of 22 min) with four ions each were used as recently described[9]. Standard solutions and sample extracts were splitless injected (1.5 min) at 225°C. The GC/MS interface temperature was set at 250°C. The non-polar capillary column CP-Sil 2 (50 m length, 0.25 mm i. d., and 0.25 μm d_f) was from Chrompack. The GC oven program was started ar 80°C (1 min), then programmed at 15°C/min to 180°C, 1.5°C/min to 250°C (5 min), and 10°C/min to 290°C (16.67 min).The GC pressure program is shown in Table 1.

Table 1: GC oven temperature, pressure program, and carrier gas flows

time [min]	temperature [°C]	pressure [psi]	carrier gas flow [cm/s]	carrier gas flow [ml/min]
0.00	80	13.2	25.5	0.80
0.10	80	13.2	25.5	0.80
0.71	80	50.0	59.2	4.33
1.00	80	50.0	59.2	4.33
1.51	87	50.0	58.4	4.19
1.95	94	23.8	34.3	1.43
7.67	180	23.8	29.5	1.00
54.32	250	29.0	30.1	1.00
59.32	250	29.0	30.1	1.00
63.32	290	29.0	28.4	0.88
80.00	290	29.0	28.4	0.88

CTT standards

Most of the measurements were performed with the "Parlar 22 components standard" (Dr. Ehrenstorfer, Augsburg, Germany) which was combined with three internal standards to a final concentration of 300 pg/µL[9]. B7-515 (Parlar #32), B7-1453, B8-1413 (Parlar #26), B8-1414 (Parlar #40), B8-1945 (Parlar #41), B8-2229 (Parlar #44), B9-1679 (Parlar #50), and B9-1025 (Parlar #62) were also combined to an eight component CTT standard at a final concentration of 100 pg/µL. Single CTT standards were from Dr. Ehrenstorfer (Augsburg, Germany) except B7-515 (Parlar #32) from Promochem (Wesel, Germany) and B7-1453 isolated by some of us[10].

3. Results and discussion

Figure 1A shows a typical GC/ECNI-MS multiple ion chromatogram of the "Parlar 22 components standard" using constant flow injection (CFI). The ECNI response factors of the CTTs varied significantly. E. g. B8-1945 (Parlar #41) had a very high response factor while the intensity of B9-1025 (Parlar #62) was very poor. Figure 1B shows the multiple ion chromatogram of the "Parlar 22 components standard" obtained with pressure pulse injection (PPI). Using PPI, the retention times of the CTTs were only marginally influenced and of excellent reproducibility (Table 2). Therefore, PPI can easily be integrated in conventional standard methods with CFI. Table 2 lists ECNI abundances of CTTs after PPI and CFI. The abundance of the early eluted B8-1413 (Parlar #26) (high vapor pressure, low boiling point) was only slightly improved with PPI, but for later eluted CTTs (decreasing vapor pressure and/or increasing boiling point) the effect on the ECNI abundance was much more pronounced. Using PPI, CTTs at medium retention times (i. e. 54 min to 59 min) yielded on average 1.5 - 2 times higher abundance. CTTs with high retention time (low vapor pressure, high boiling point) showed more than three times higher abundance. This led to the fact that B9-2206 (Parlar #63) dominated the PPI-chromatogram (Figure 1B) while B8-1945 (Parlar #41) dominated the CFI-chromatogram (Figure 1A). Note that the increment of abundance of a CTT obtained by PPI was constant for all monitored ions (Table 2). Therefore, the high pressure pulse during the injecton did not increase decomposition of the CTTs. This is in agreement with findings of Wylie et al. who studied the stability of DDT with both PPI and CFI[6]. PPI significantly increased the abundance of B9-1025 (Parlar #62) relative to B8-1413 (Parlar #26) and B9-1679 (Parlar #50). E. g., the percentage ratio of most abundant ion of B9-1025 (Parlar #62) and B8-1413 (Parlar #26) was 3% using CFI and 11% using PPI.

Table 2: ECNI-MS abundances of six m/z values of important CTTs after constant flow injection (CFI) and pressure pulse injection (PPI)

CTT	mode	RT [min]	m/z 340.9	m/z 342.9	m/z 376.9	m/z 378.9	m/z 410.8	m/z 412.8
B8-1413	CFI	47.70	1168 [2]	1372	**6019** [3]	5766	-	-
(Parlar #26)	PPI	47.71	1313	1592	**6755**	6493	-	-
	incr. [1]		(1.12)	(1.16)	**(1.12)**	(1.13)	-	-
B7-515	CFI	50.34	1711	**3272**	-	-	-	-
(Parlar #32)	PPI	50.35	2854	**5531**	-	-	-	-
	incr.		(1.67)	**(1.69)**	-	-	-	-
B8-1414	CFI	54.64	1664	1648	**5997**	5762	-	-
(Parlar #40)	PPI	54.64	2828	2844	**9836**	9573	-	-
	incr.		(1.69)	(1.70)	**(1.64)**	(1.66)	-	-
B8-1945	CFI	55.11	486	794	**12621**	12186	-	-
(Parlar #41)	PPI	55.12	791	1315	**20950**	20220	-	-
	incr.		(1.63)	(1.66)	**(1.66)**	(1.66)	-	-
B8-2229	CFI	56.59	742	954	**3725**	3563	-	-
(Parlar #44)	PPI	56.59	1443	1816	**7186**	6884	-	-
	incr.		(1.94)	(1.90)	**(1.93)**	(1.93)	-	-
B8-1679	CFI	58.52	1101	652	776	563	3825	**4100**
(Parlar #50)	PPI	58.51	2012	1208	1414	1006	7186	**7701**
	incr.		(1.83)	(1.85)	(1.82)	(1.79)	(1.88)	**(1.88)**
B9-1025	CFI	64.04	107	102	**178**	135	59	62
(Parlar #62)	PPI	64.16	483	414	**811**	613	257	283
	incr.		(4.51)	(4.06)	**(4.56)**	(4.54)	(4.36)	(4.56)
B9-2206	CFI	64.52	2815	2250	947	774	6129	**6562**
(Parlar #63)	PPI	64.67	9303	7608	3217	2629	21096	**22658**
	incr.		(3.30)	(3.38)	(3.40)	(3.40)	(3.44)	**(3.45)**

1) increment = ratio of the abundance of PPI to CFI
2) 1/1000 of the value, measured by the instrument's integrator
3) values printed bold are the most abundant ECNI mass fragment ions of CTTs

4. Conclusions.

Using PPI the abundance of CTTs with a low ECNI response factor such as B9-1025 (Parlar #62) can be decisively increased. The PPI will also beneficial in GC/ECD analysis. Furthermore, the technique can be simplyfied by programming only the injection followed by constant flow.

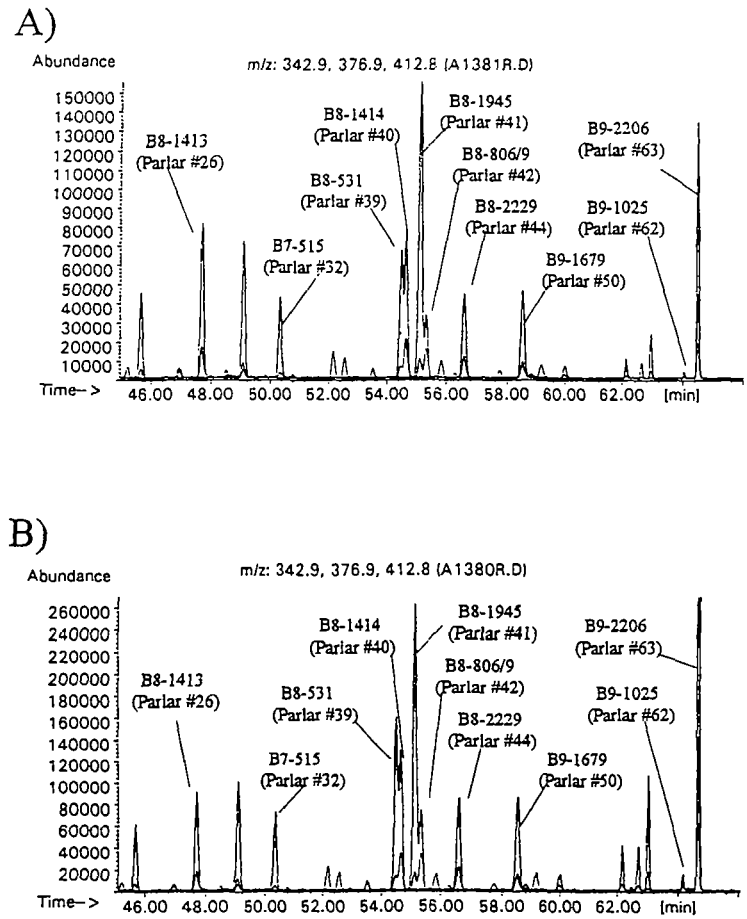

Figure 1: GC/ECNI multiple ion chromatogram of the Parlar 22 components standard A) constant flow splitless injection; B) pressure pulse splitless injection

5. References.

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