

The effects of perfluorotributylamine (PFTBA) concentration on ECNI mass spectrometer tuning conditions and its influence on instrument sensitivity

Jiping Zhu¹ and Ross J. Norstrom²

¹ JP Ztech Company, 6058 Pineglade Crescent, Gloucester, Ontario Canada K1W 1H1

² Canadian Wildlife Service, Environment Canada, Hull, Quebec Canada K1A 0H3

Introduction

Electron capture negative ionization mass spectrometer (ECNI/MS) has become a standard technique for the analysis of toxaphene (polychlorocamphenes) due to its high sensitivity and specificity¹⁾. Although some problems associated with toxaphene analysis using ECNI/MS have been addressed²⁾, and the ECNI conditions, such as source temperature, ECNI reagent gas pressure have been discussed³⁾, the influence of the concentration of the ECNI tuning agent, perfluorotributyl-amine (PFTBA) in the ion source chamber has been largely ignored so far. The present paper presents the results of our investigation on the effects of different levels of PFTBA on the optimal tuning conditions and its relation to toxaphene analyses.

Experimental

Toxaphene standard, a mixture of 11 congeners at 66.6 pg/ μ L per congener with known structure⁴⁾ was obtained from Professor Dr. H. Parlar at the toxaphene workshop held at Burlington, Canada in February 1993. The standard was diluted with hexane to 26.64 pg/ μ L and 5.33 pg/ μ L respectively.

The experiment was carried out on a Hewlett-Packard (HP) 5985 mass spectrometer (MS) upgraded with an HP 5980 series II gas chromatograph (GC) and an HP 5988 GC/MS direct interface. ECNI mode was operated at an ion source temperature of 130 °C and an optimal ion source pressure of about 0.5 bar adjusted by the flow of methane reagent gas. The instrument was manually tuned with PFTBA at ions m/z 312, 414 and 595, first when the PFTBA valve was completely open to obtain the high concentration and then when it was closed to create a low concentration of PFTBA. Samples were analyzed under these two different tuning conditions while all other experimental conditions were kept the same.

The Dwell time of each of the ions in selected ion monitoring (SIM) mode was 100 ms. M/z 341 & 343, 377 & 379, 411 & 413, and 447 & 449 were selected to monitor hept-, octa-, nona- and deca-

ANA/BIOA

chlorinated toxaphene isomers respectively. The GC conditions were as follows: DB-5 capillary column, 30 m x 0.25 mm i.d. fused silica with 0.25 μm film thickness; carrier gas, helium; purge on, 1 min; splitless injection, 2 μL at 260 °C; Oven temperature was 60 °C (2 min), 20 °C/min to 220 °C and 3 °C/min to 260 °C (5 min). The temperature of the transfer line was 280 °C.

Results and Discussion

Although it is difficult to measure the actual concentration of the PFTBA in the ion source chamber, the concentration level of the PFTBA can be monitored by the abundance of ions appearing in either the repeated scan window (representing full scan mode) or in the ramp spectrum (representing SIM mode). The concentration of PFTBA was considered "high" when the PFTBA valve was open. This level of PFTBA is useful to adjust the peak width and mass scale. When the valve was closed, the level of PFTBA in the ion source chamber decreased, but a background "low" concentration of PFTBA remained for several hours.

Under our experimental conditions, it was observed that the optimal value of each tuning parameter of the HP 5988 instrument in ECNI mode depended on the amount of PFTBA in the ion source chamber. Since toxaphene congeners with six ($M\text{-Cl} = 307$) to nine ($M\text{-Cl} = 409$) chlorines are dominant ones in the environment, the optimal conditions were chosen based on maximum abundance of m/z 312 and m/z 414. As demonstrated in Figure 1a and 1b, the optimal value for the repeller shifted from about 9 to 10 volt at high PFTBA concentration (abundances of m/z 414 and 312 are 93,800 and 18,700, respectively) to about 4 to 5 volt at low concentration (abundances of m/z 414 and 312 are 17,400 and 3,170, respectively). A similar shift, from around 170 volt to about 110 volt, was observed in ion focus ramp. Other parameters such as electron energy, entrance lens and draw out also changed slightly (ramp curves are not presented in this paper). The function of the repeller is to push negative ions from the ion chamber into the analyzer (quadropole), and the function of the ion focus is to concentrate and align the ion beam entering the analyzer. The different optimal values of the tuning parameters resulting from tuning at high and low PFTBA concentrations will affect the instrument sensitivity.

ECNI/MS is a sensitive instrument to measure toxaphene residues in various environmental and biological samples. An instrument detection limit of 1 picogram (pg) or less per congener is achievable for most ECNI/MS. However, the optimal tuning conditions based on high PFTBA concentration may not be the best condition for analyzing this trace level of toxaphene compounds. This was demonstrated in the present study by analyzing toxaphene standards at two low pg levels (26.64 pg/ μL and 5.33 pg/ μL , 2 μL injection).

The response factors (RF, defined as peak area per pg per compound) of each peak resulting from the tuning conditions obtained at both high and low PFTBA concentration are summarized in Table 1. When 53.3 pg of each congener was injected into the instrument, the average RF obtained from tuning with high PFTBA concentration was 0.66 ± 0.03 of the RF from tuning with low PFTBA concentration. This ratio was further reduced to 0.57 ± 0.05 when a smaller amount (10.6 pg) was injected. Due to the fast GC program (25 min), the peaks of compound 7 and 8, and 10 and 11 were merged. They can be separated with a longer run program.

The linearity of response factors over the range of 10.6 pg to 53.3 pg was much better for most hepta-, octa- and nona-chloro isomers under the tuning conditions obtained from low PFTBA

concentration, that is, the ratios of the RFs at 53.3 pg to those at 10.6 pg were closer to 1.0 (Table 1). Under the tuning conditions obtained from low PFTBA, the RF ratios of hept-, octa- and nona-chlorinated isomers were 1.06 ± 0.05 , except for compound 6, which was 1.42. The RF ratios were higher (1.17 ± 0.06) when the instrument was tuned with high PFTBA concentration. The RF ratios for decachloro isomers were >2 in both cases, probably due to low abundance (poor ion statistics) at the 10.6 pg level, indicating significant non-linear response under all conditions.

Table 1: ECNI/MS response factors (Area/pg) of toxaphene congeners resulting from tuning with high and low PFTBA concentrations in the ion chamber.

Compound	#Cl	Standard (53.3 pg)			Standard (10.6 pg)			RF Ratio*	
		High	Low	High/low	High	Low	High/low	High	Low
1	8	2350	3659	0.64	2071	3449	0.60	1.13	1.06
2	7	2804	4294	0.65	2403	3893	0.62	1.17	1.10
3	8	5277	8022	0.66	4421	7284	0.61	1.19	1.10
4	9	1855	2835	0.65	1715	2917	0.59	1.08	0.97
5	9	3321	4797	0.69	2889	4541	0.64	1.15	1.06
6	9	1473	2279	0.65	839	1610	0.52	1.76	1.42
7+8**	9	6972	11072	0.63	5476	10366	0.53	1.27	1.07
9	10	519	773	0.67	195	372	0.52	2.67	2.08
10+11**	10	1018	1398	0.73	227	463	0.49	4.49	3.02

* RF ratio is defined as RF at 53.3 pg level divided by that at 10.6 pg level.

** Merged peak. RF is based on 106.6 pg and 21.2 pg respectively.

References

- 1) Special edition of papers presented at the Toxaphene Workshop at Burlington, Canada in February 1993 (1993) *Chemosphere* **27**(10).
- 2) Lau, B., Weber, D. and Andrews, P. (1994) *Rapid Communications in Mass Spectrometry* **8**, 849 - 853.
- 3) Stemmler, E.A. and Hites, R.A. (1985) *Anal. Chem.* **57**, 684 - 692.
- 4) Burhenne, J., Hainzl, D., Li Xu, Vieth, B., Alder, L. and Parlar, H. (1993) *Fresenius J. Anal. Chem.* **346**, 779 - 785.

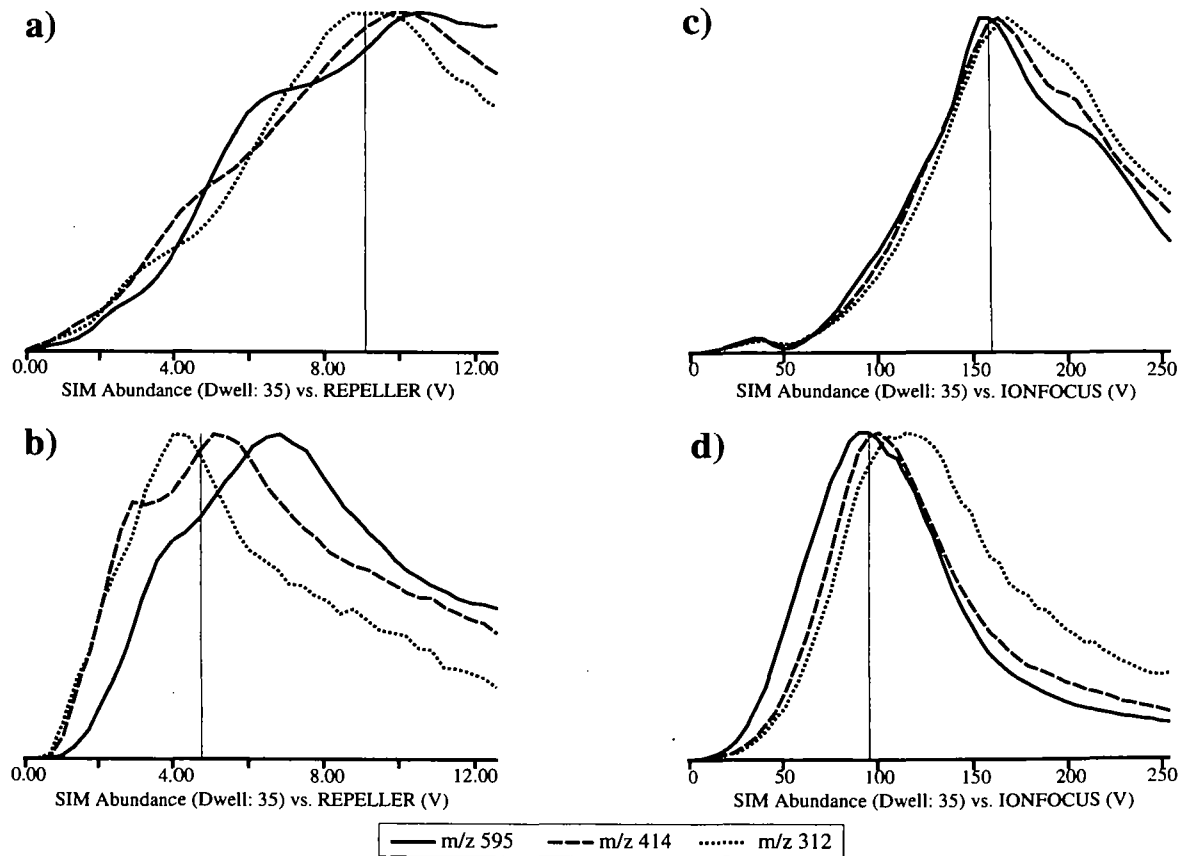


Figure 1. Ramp curves of a) repeller at high PFTBA concentration; b) repeller at low PFTBA concentration; c) ion focus at high PFTBA concentration; and d) ion focus at low PFTBA concentration.