Mass spectrometry analysis of polychlorinated biphenyls: chemical ionization and selected ion chemical ionization using methane as a reagent gas*

TATJANA M. VASILJEVIĆ,[1**] MILA D. LAUŠEVIĆ[1**] and RAYMOND E. MARCH[2]

[1]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Yugoslavia and* [2]*Trent University, Peterborough, ON K9J 7B8, Canada*

In the present paper a quadrupole ion trap mass spectrometer, coupled with a gas chromatograph, was used to compare the electron impact ionization (EI) and chemical ionization (CI) technique, in terms of their selectivity in polychlorinated biphenyls (PCBs) quantitative analysis. The experiments were carried out with a modified Varian SATURN III quadrupole ion-storage mass spectrometer equipped with Varian waveform generator, coupled with a gas chromatograph with DB-5 capillary column. The disadvantage of using EI in the analysis of PCBs congeners is the extensive fragmentation of the molecular ion. The main fragmentation pattern recorded in the EI mass spectra of PCBs was the loss of a chlorine atom from the molecular ion. Therefore the fragment-ion signal overlapped with the molecular-ion cluster of lower mass congener. The fragmentation reactions of PCBs are suppressed if methane is used as a reagent gas for chemical ionization, but fragment ions are also present in the spectrum as an obstruction for quantitative analysis. The most selective method for PCBs quantitative analysis appears to be CI with mass-selected $C_2H_5^+$ ions from methane, which results in a mass spectrum with a negligible amount of fragment ions.

Keywords: ion trap, mass spectrometry, electron impact ionization, chemical ionization, selected ion chemical ionization, polychlorinated biphenyls, Aroclor.

INTRODUCTION

Polychlorinated biphenyls (PCBs), common environmental pollutants, exist as 209 congeners according to the number and positions of the chlorine atoms.[1] PCBs differ widely in their physicochemical properties, toxicity and their distribution within the environment. The toxicity of PCB mixtures is due primarily to a small group of non-*ortho* and mono-*ortho* substituted congeners.[2] Therefore it is important to measure PCBs on a congener-specific basis.

The identification and quantification of PCBs can be difficult because they were often used in complex mixtures (Aroclor[TM], Chlorophen[TM], Kannechlor[TM],

---

* Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday

** Serbian Chemical Society active member

Fenclor[TM], *etc.*) and the composition of PCB-containing samples in the environment changes due to natural degradation processes. The most commonly used analytical technique for PCBs analysis has been high-resolution gas chromatography with electron capture or mass-selective detectors.[1,3] The major analytical problems affecting the quantitative determination of PCBs are: co-elution of the congeners, the low concentration of more toxic (non-*ortho* substituted) congeners relative to other PCBs in the environment and nonlinear detector response to congeners containing a different number of chlorine atoms.

In the present paper a quadrupole ion trap mass spectrometer, coupled with a gas chromatograph, was used to compare the electron impact ionization (EI) and chemical ionization (CI) technique in the terms of their selectivity in the quantitative analysis of PCBs. Methane was used as a CI reagent. The isolation and subsequent reaction of $C_2H_5^+$ ions from methane was employed. The work carried out in this study is part of a program on the application of ion trap mass spectrometry to the development of analytical protocols for PCBs.

EXPERIMENTAL

The experiments were carried out with a modified Varian SATURN III Quadrupole Ion Storage Mass Spectrometer (QISMS[TM]) coupled with a gas chromatograph and equipped with both a Varian waveform generator and Varian 8200 autosampler. The technical details of the operation of the instrument under both EI and standard Cl conditions, as well as the isolation of a specific CI reagent ion have been described previously.[4,5]

A 30 m DB-5 capillary column (0.25 nm i.d., 0.25 μm film thickness) was used with helium flow adjusted to give a column head pressure of 12 psi. The injector temperature was 220 °C. The column was held at 38 °C during the sample injection, then ramped to 260 °C at 20 °C min^{-1} and held at that temperature for 10 min. The transfer line temperature was held at 220 °C.

The commerical PCBs mixture Aroclor 1254, obtained from Supelco, Inc., Bellefonte, USA was used in this study. The mixture was diluted with *iso*-octane to a concentration of 10 μg ml^{-1}.

RESULTS AND DISCUSSION

Electron impact ionization

Figure 1 shows the total ion chromatogram (a) and the mass chromatograms (b) and (c) of the most abundant ions in the molecular isotope cluster of tetra- and pentachlorobiphenyl congeners, respectively, obtained using the EI mode. It can be noticed that the chromatograms in Fig. 1b and c have similar patterns. We assumed that some of the peaks observed in the upper chromatogram (supposed to be molecular ions of tetrachlorobiphenyl congeners) might be the result of fragmentation of pentachlorocongeners present in the lower chromatogram. The unresolved peak, marked with *, containing congeners with four and five chlorine atoms, was analyzed. Based on published relatve retention times of congeners in Aroclor 1254,[6] on a slightly different column phase (DB-1), we estimated that the marked GC peak contains congeners 66 and 95, having one chlorine atom in the *ortho* position (more toxic) and three clorine atoms in the *ortho* position, respectively. The elution order of PCB congeners depends on the number of chlorine atoms (increasing number of
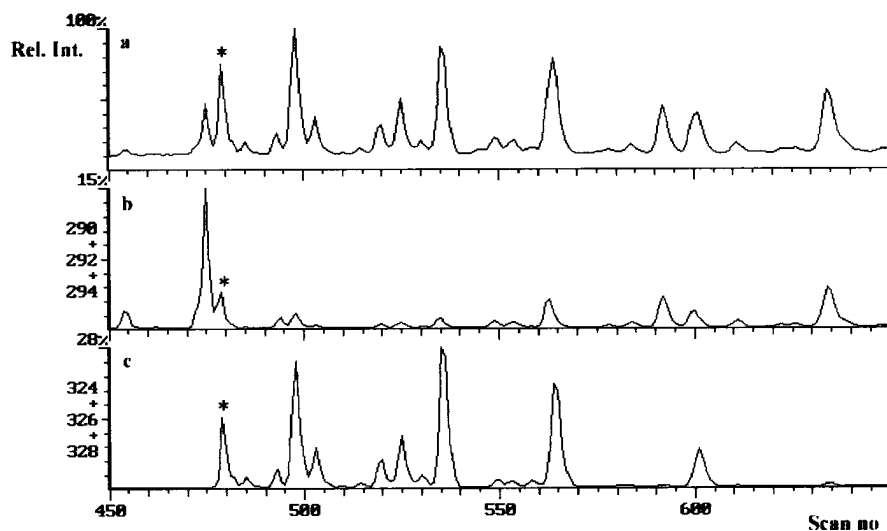
Fig. 1. EI chromatograms of Aroclor 1254: a) total ion chromatogram, b) molecular cluster mass chromatogram of tetrachlorobiphenyl isomers and c) molecular cluster mass chromatogram of pentachlorobiphenyl isomers.

Cl atoms increase retention time) and the number of chlorine atoms in the *ortho* position (increasing number of Cl *ortho* substituents increase retention time).[3,6,7] Therefore, it is a common analytical problem that non-*ortho* and mono-*ortho* substituted congeners co-elute with congeners containing one more chlorine atom in the molecule. An example for such behavior is the marked GC peak in Fig. 1.
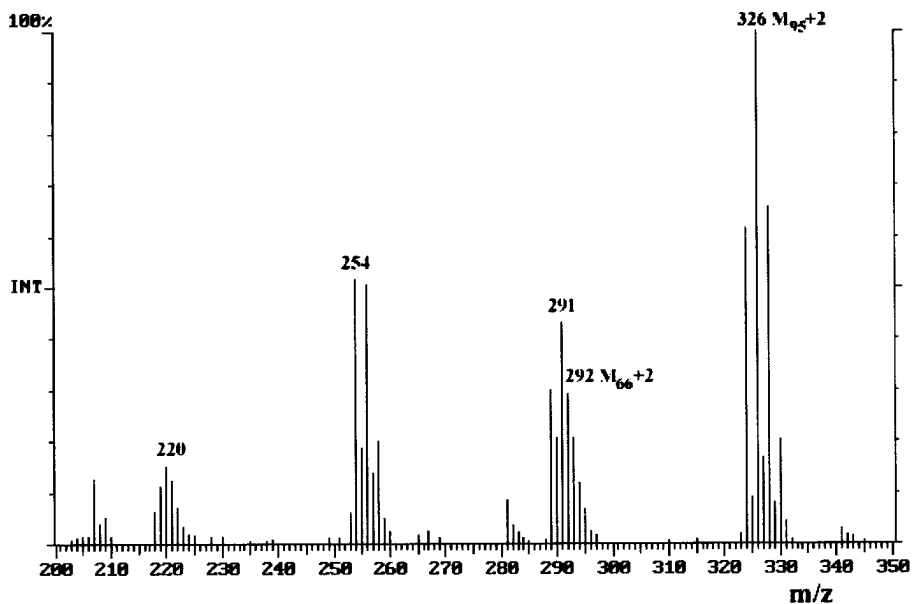

Fig. 2. Electron impact mass spectrum of the co-eluting polychlorinated biphenyl congeners 66 and 95.

TABLE I. Ratio of the relative intensity of molecular ions for congeners 66 and 95

Ionization technique	Relative intensity $M*_{95} : M*_{66}$
Electron impact	100:29
Chemical ionization (methane as the reagent gas)	100:17
Selected ion chemical ionization ($C_2H_5^+$ ion from methane as the reagent cation)	100:10

$M*_{95}$ - the most prominent ion in the molecular ion cluster of congener 95
$M*_{66}$ - The most prominent ion in the molecular ion cluster of congener 66

The composite EI mass spectrum for the marked peak is shown in Fig. 2. The base peak group in the mass spectrum is the molecular ion cluster of the pentachlorocongener 95, where m/z 326 is $[M_{95}+2]^+$, and it shows the expected isotope pattern. The fragment ion cluster due to the loss of one chlorine atom from congener 95, with the most pronounced signal at m/z 291 $[M_{95}-Cl+2]^+$, is superimposed on the molecular ion cluster of the tetrachlorocongener 66 (m/z 292 $[M_{66} + 2]^+$). The composite peak group is characterized by an irregular isotope pattern. Therefore, the quantitative determination of congener 66 in the presence of congener 95 is not possible using the EI technique. The fragment ion clusters formed by the loss of two chlorine atoms from the molecular ion of congener 95, m/z 256 $[M_{95}-2Cl+2]^+$, and congener 66, m/z 220 $[M_{66}-2Cl+2]^+$, also show an irregular isotope pattern. The relative intensity ratio for molecular ions $[M_{95} + 2]^+/[M_{66} + 2]^+$ for all experiments is shown in Table I. In this case the relative intensity ratio is 100:29.
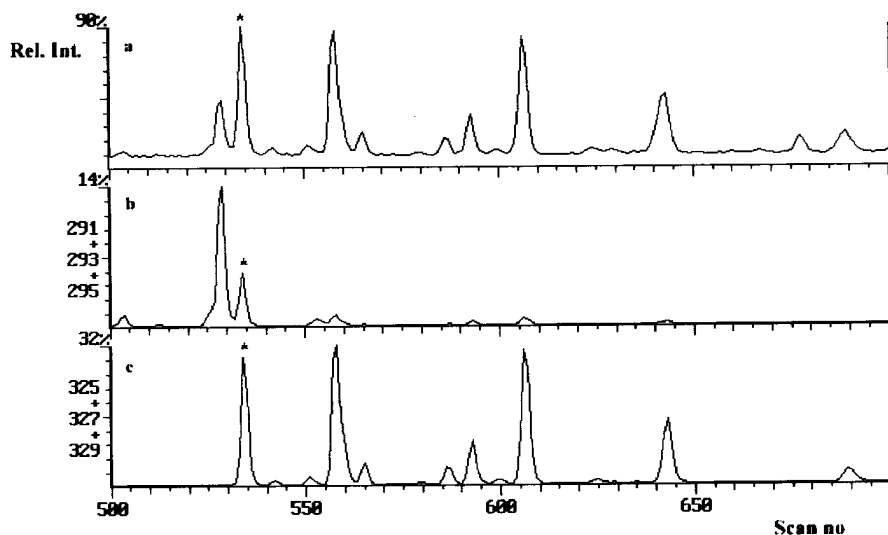

Fig. 3. CI chromatograms of Aroclor 1254: a) total ion chromatogram, b) molecular cluster mass chromatogram of tetrachlorobiphenyl isomers and c) molecular cluster mass chromatogram of pentachlorobiphenyl isomers, using methane as the ionization reagent gas.

Chemical ionization

Figure 3 shows the total ion chromatogram (a) and mass chromatograms (b) and (c) of the most abundant ions in the molecular isotope cluster of tetra- and pentachlorobiphenyl congeners, respectively, obtained using the CI mode with methane as a reagent gas. The chromatogram of tetrachlorobiphenyls is less influenced by the fragmentation of pentachlorobiphenyls compared to the EI chromatograms.
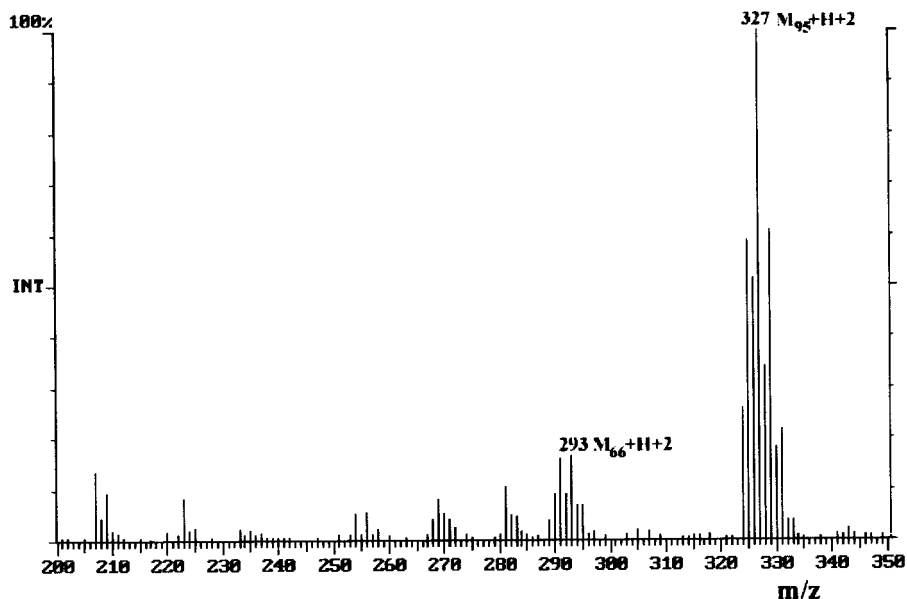

Fig. 4. Chemical ionization mass spectra of the co-eluting polychlorinated biphenyl congeners 66 and 95, using methane as the ionization reagent gas.

When methane was used as the CI reagent gas, the dominant features in the mass spectrum (Fig. 4) are the protonated molecular ion clusters of each congener, where m/z 327 is $[M_{95} + H + 2]^+$ and m/z 293 is $[M_{66} + H + 2]^+$. In each case the chlorine isotope pattern is distorted due to superimposition of charge exchange reactions and protonation. The contribution of the summed fragment ion current is less than 20 % of the total ion current. The relative intensity ratio for the molecular ions $[M_{95} + H + 2]^+/[M_{66} + H + 2]^+$ is 100:17. We suppose that it is a more accurate ratio than one obtained from the EI spectra because the intensity of the molecular ion of congener 66 is less influenced by the fragmentation of congener 95.

Selected reagent ion

For our study, the reagent ion $C_2H_5^+$ from methane was selected, stored in the ion trap for a sufficiently long time to react with the Aroclor 1254 eluting from the GC column. The resulting total ion and selected ion chromatograms are shown in Fig. 5. The middle trace, Fig. 5b, does not follow the lower pentachlobiphenyls trace (Fig. 5c), suggesting that fragmentation has a negligible influence. The co-eluting congeners, as the one marked with *, can be clearly recognized.
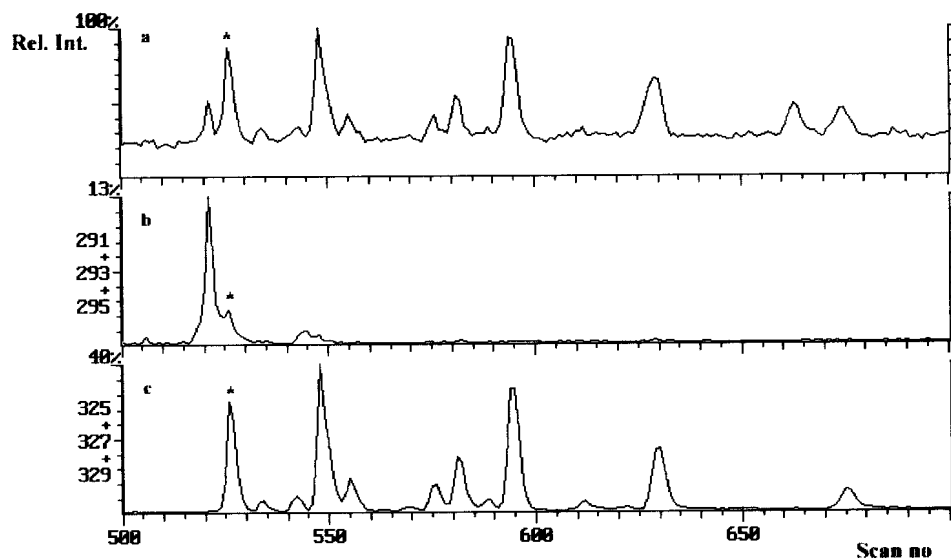
Fig. 5. Selected ion CI chromatograms of Aroclor 1254: a) total ion chromatogram, b) molecular cluster mass chromatogram of tetrachlorobiphenyl isomers and c) molecular cluster mass chromatogram of pentachlorobiphenyl isomers, using $C_2H_5^+$ from methane as the reagent ion.

The MS spectrum obtained from the marked GC peak is shown in Fig. 6. The dominant species are protonated molecular ion clusters. The molecular clusters
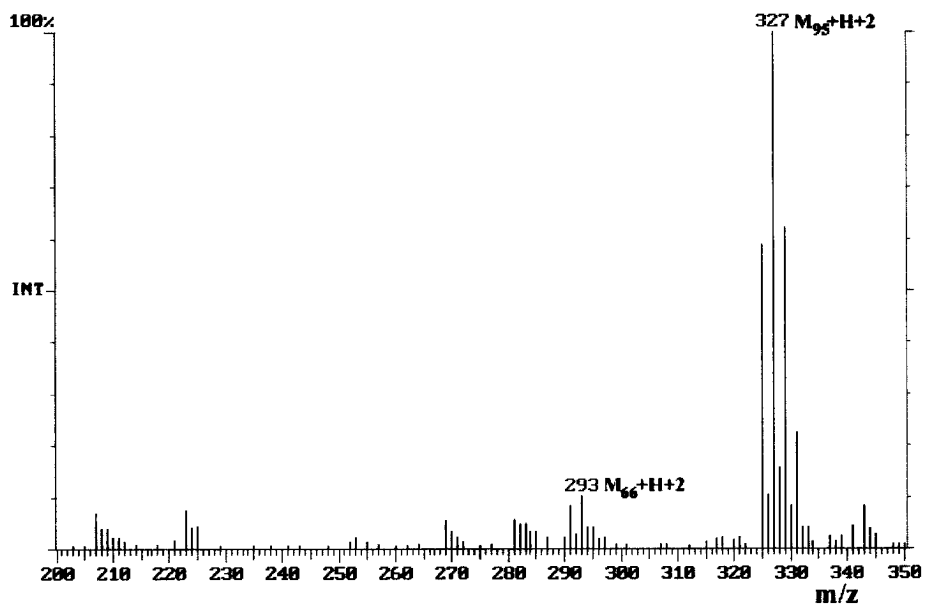

Fig. 6. Selected reagent ion chemical ionization mass spectrum of the co-eluting polychlorinated biphenyl congeners 66 and 95 using $C_2H_5^+$ from methane as the reagent ion.

exhibit the expected isotope patterns. The influence of charge exchange reactions and fragmentation are negligible. The relative intensity ratio for the molecular ions $[M_{95} + H + 2]^+/[M_{66} + H + 2]^+$ is 100:10. This is the lowest molecular intensity ratio obtained in our experiments, suggesting the lowest contribution of fragment ion cluster of congener 95 to the intensity of the molecular ion cluster of congener 66. The molecular ion intensity ratio, in this case, represents the relative molar concentration of the congeners 95 and 66 in the mixture. Therefore, it can be assumed that the ion $C_2H_5^+$ has a potential analytical application for the quantitative analysis of PCBs.

CONCLUSIONS

The disadvantage of using EI in the analysis of PCB congeners is the extensive fragmentation of the molecular ion. The main recorded pattern in the EI mass spectra of PCBs was the loss of a chlorine atom from the molecular ion. Therefore the fragment-ion signal overlapped with the molecular-ion cluster of the lower mass congener. The principal reactions observed during CI were protonation, charge exchange and fragmentation. The advantage of the ion-trap detector lies in its capability to isolate a selected ion as a CI reagent. The most selective method for PCBs quantitative analysis appears to be CI with mass-selected $C_2H_5^+$ ions from methane, resulting in a mass spectrum with a negligible amount of fragment ions and a negligible influence of charge exchange.

И З В О Д

МАСЕНО СПЕКТРОМЕТРИЈСКА АНАЛИЗА ПОЛИХЛОРОВАНИХ БИФИНИЛА: ХЕМИЈСКА ЈОНИЗАЦИЈА И ХЕМИЈСКА ЈОНИЗАЦИЈА ОДАБРАНИМ ЈОНОМ МЕТАНА

ТАТЈАНА М. ВАСИЉЕВИЋ,[1*] МИЛА Д. ЛАУШЕВИЋ[2] и RAYMOND E. MARCH[2]

[1]*Технолошко-металуршки факултет, Карнегијева 4, 11000 Београд* и [2]*Trent University, Peterborough, ON K9J 7B8, Kanada*

У овом раду помоћу квадрополног масеног спектрометра са јонским трапом у спрези са гасним хромотографом вршено је поређење техника електронске и хемијске јонизације, уз коришћење метана као јонизујућег реагенса, у погледу селективности за квантитативну анализу PCB-а. Експерименти су вршени на Варијановом модификованом квадрополном спектрометру са јонским трапом SATURN III опремљеним генератором таласа у спрези са гасним хроматографом са DB-5 капиларном колоном. Недостатак методе електронске јонизације је интензивна фрагментација молекулског јона. Како су главни производи фрагментације јони настали губитком атома хлора из молекулског јона, долази до преклапања пикова фрагментних јона са кластерима молекулских јона хомолога мање молекуслке масе. Када је метан коришћен као јонизујући реагенс фраг-ментација је смањена, али су фрагментни јони и даље присутни у спектру што има утицај на резултате квантитативне анализе. Метода за квантитативно одређивање PCB-а која се по селективности издваја од осталих је хемијска јонизација са $C_2H_5^+$ јоном издвојеним

из метана, којом је добијен масени спектар са занемарљивом количином фрагментних јона.

REFERENCES

1. *Environmental Health Criteria 140: Polychlorinated Biphenyls and Terphenyls*, World Health Organization, Geneva (1993) 44-79
2. S. Safe, *Environ. Health Persp.* **100** (1992) 259
3. G. Font, J. Manes, J. C. Molto, Y. Pico, *J. Chromatogr. A* **733** (1996) 449
4. J. B. Plomley, C. J. Koester, R. E. March, *Anal. Chem.* **66** (1994) 4437
5. M. Lausevic, J. B. Plomley, X. Jiang, R. E. March, *Eur. Mass Spectrom.* **1** (1995) 149
6. A. Buthe, E. Denker, *Chemosphere* **30** (1995) 753
7. M. Bolgar, J. Cunningham, R. Cooper, R. Kozloski, J. Hubball, *Chemosphere* **31** (1995) 2687.