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Optimization and application of high-resolution gas chromatography with ion trap tandem mass spectrometry to the determination of polychlorinated biphenyls in atmospheric aerosols

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Abstract

Optimization of the Finnigan GCQ ion trap mass spectrometry (ITMS) system and a clean-up procedure were carried out in order to apply high-resolution gas chromatography–tandem mass spectrometry for the analysis of polychlorinated biphenyls (PCBs) in aerosols. Six ITMS operating parameters, including isolation time, excitation voltage, excitation time, ''*q*'' value, ion source temperature and electron energy were adjusted in order to optimize the instrument analytical performance. The adjustment of all parameters substantially increased the sensitivity of ITMS in the MS–MS mode. Changes in isolation time did not particularly affect ITMS sensitivity while ion source temperature had the strongest influence. After optimization, a limit of detection of 600 fg/μl with S/N varying from 8 up to 91 was achieved. The application of the optimized ITMS parameters conjointly with the developed clean-up procedure resulted in method detection limits of 10–20 fg/m^3 for the determination of PCBs, in the particulate and gas phase of the atmospheric aerosol of background areas in the Eastern Mediterranean and Sweden.

Keywords: Aerosols; Air analysis; Environmental analysis; Polychlorinated biphenyls

1. Introduction

Persistent organic pollutants (POPs) constitute a large heterogeneous group of compounds with a broad range of physical, chemical and ecotoxicological properties. In 1998, different nations, under the auspices of the United Nations Environment Programme (UNEP), began negotiations on a binding global agreement to prohibit, restrict, or reduce the production, use, or release of certain POPs [1]. Risks posed by POPs may occur far from the site of initial emission into the environment and include effects in remote, polar, and oceanic regions of the planet. Wania and Mackay have suggested that several organochlorine POPs can be transported at the polar region through a global fractionation and cold condensation process [2]. In 1995 UNEP established the first list of 12 substances or substance groups selected for global action [DDT, dieldrin, aldrin, endrin, mirex, chlordane, heptachlor, toxaphene, hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs)] [1].

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PCBs constitute a substance group included in the first UNEP list [1]. PCBs are ubiquitous environmental contaminants and their presence has been confirmed for a variety of environmental matrices such as water [3–7], soil [8–10], sediments [11,12], vegetation [13–15] and mammal tissues [16,17] all over the world. The interest in these compounds is not only due to their toxic effects on biota [18] but also due to their chemical stability in the environment [10,19] and their ability to transport to the most remote areas [2,20–22].

Redundant high-resolution gas chromatography (HRGC) with electron-capture detection (ECD) is still a widely utilized analytical technique for the trace analysis of PCBs in various environmental matrices. ECD, as a detection method, has some advantages such as specificity for halogenated compounds, high sensitivity, very low detection limit, ease of operation and maintenance. However, ECD is unable to differentiate between PCBs and coeluting interferences like 4,4′-DDE [23], and more seriously, cannot resolve PCB congener pairs like congeners 77 and 110 [24]. Electron-capture detectors also suffer from non-linear response behavior across a relatively narrow amount range and wide variation in response within a PCB homologue group [25]. This fact often forces analysts to reanalyze samples or to use nonlinear functions to calibrate the ECD system [26]. Moreover, a disadvantage of ECD due to the absence of substantial qualitative data is the identification of PCBs congeners solely on retention time.

The use of mass spectrometry (MS) detection in the electron ionization (EI) mode increases selectivity and enhances the analyte identification potential conjointly with the GC retention time information. However, the determination of PCBs by conventional EI-MS, even in the selected ion-monitoring (SIM) mode, exhibits higher detection limits than ECD [27]. The main alternative MS techniques currently used for analysis of PCBs at trace level are negative chemical ionization mass spectrometry (NCI-MS) [28–30] and high-resolution mass spectrometry (HRMS) [31,32]. Usually, both techniques provide much higher sensitivity than EI-MS but the complexity of use, the high cost for purchase and maintenance constitute disadvantages that restrict their use in routine analysis of PCBs.

Recently, tandem mass spectrometry (MS–MS) analysis by ion trap mass spectrometry (ITMS) systems became a competitive technique for the determination of PCDD/Fs [33,34] and PCBs [35]. In order to attain low detection limits, the instrumental parameters of ITMS must be thoroughly optimized. Despite the use of ITMS for the determination of PCBs in biota and sediments by the MS–MS technique, there is not a systematic study related to the instrumental parameters, affecting the performance of this system.

In recent years it was established [2,20–22] that the gas/particle partitioning of PCBs in the atmosphere determines the extent of their global transportation. The scarcity of results from remote areas is due to difficulties in the determination of the low PCB concentrations in the gas and even lower concentrations in the particulate phase. The aim of the present study was to establish an overall analytical method, including a clean-up procedure and an optimization of a set of instrumental parameters, in order to attain the highest possible sensitivity for the determination of PCBs in atmospheric aerosol samples. Particular attention was paid to the optimization of six ITMS parameters, namely isolation time, excitation voltage, excitation time, ''q'' value, ion source temperature and electron energy. Other operating parameters of ITMS, like automatic gain control (AGC) target value or emission current, were not adjusted since, according to the supplier (Finnigan) instructions, the resolution and mass accuracy and the operation performance of the instrument could be reduced. For these parameters the default values were used. In order to improve ITMS specificity (e.g., decrease of potential interference from ''non-PCB'' ions) the isolation width of the precursor ion and the product ions m/z range were reduced to the lowest possible values.

The established method was then applied to determine PCBs at trace levels (pg or fg/m^3) in the gas and particulate phase of background atmospheric aerosols in Sweden and, for the first time to our best knowledge, in two sites in the Eastern Mediterranean.

2. Experimental

2.1. Materials

Standard solutions of 23 PCBs (18, 28, 52, 54, 70,

155, 90, 101, 110, 116, 123, 118, 149, 153, 132, 105, 138, 158, 160, 180, 185, 199 and 194) were purchased from Ehrenstorfer (Augsbourg, Germany). Toluene, acetone and *n*-hexane were purchased from Merck (Darmstadt, Germany). Glass fiber filters were purchased from Whatman (Maidstone, UK) and polyurethane foam plugs from Som & Sunde Skumplastfabrikk (Norway).

2.2. ITMS parameter optimization

The Finnigan GCQ gas chromatograph equipped with a 30 m×0.25 mm, 0.25 μm film thickness, HP-5MS fused-silica column (with siloxane stationary phase) was directly interfaced to a Finnigan ITMS detector. All injections (2 μl) were made using the ''hot-needle'' technique in the splitless mode (split was open after 0.8 min) and the temperature program of the oven was as follows: 95°C for 0.8 min, 3.5°C/min to 290°C. The temperatures of the injector and transfer line were kept constant through all injections at 250 and 290°C, respectively. Helium was used as carrier gas at a constant linear gas velocity of 35 cm/s. By using these chromatographic conditions, the separation of PCB 153 from PCB 132 and of PCB 138 from PCBs 160+158 was feasible (Fig. 1).

The first step of the MS–MS optimization procedure was the selection of an appropriate precursor ion for each PCB congener. A mixture of the 23 PCBs was prepared in toluene and injected in the GC–ITMS operating in full scan mode. The most abundant ion, from each congener's full scan spectrum, was selected as the precursor ion for the sequential application of MS–MS. After the application of the second ionization step (collision-induced dissociation or CID) to parent ions, the MS–MS spectrum was obtained for each PCB congener. Two product ions were then selected, on the basis of highest abundance, as the characteristic ions for each congener. For the MS–MS experiment described above, the default values for all operating parameters of the ITMS system were set. These were 200°C for ion source temperature, 1.0 u for the isolation width, 8 ms for isolation time, 15 ms for excitation time, 5 V for excitation voltage, 15 ms for excitation time, 0.3 for ''*q*'' value, 50 for AGC target value, 70 eV electron energy and 250 mA for the emission current. The instrument «automatic tune» procedure set the electron multiplier voltage, to achieve a combined gain for the conversion dynode and electron multiplier of 300 000. The mass range, at this stage of the MS–MS experiment, was m/z 10 to m/z 650 in order to detect all possible product ions.

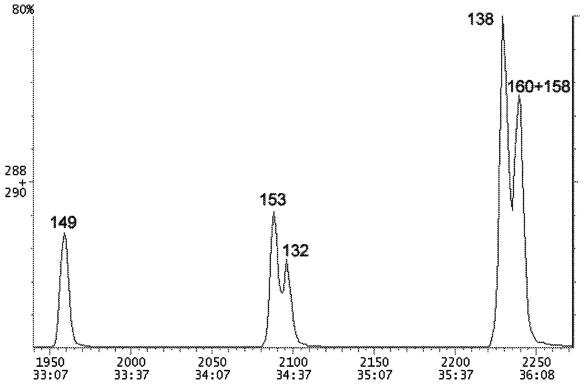

Fig. 1. Separation of PCBs 153, 132 and 138, 160+158 in a HP5-MS column.

To optimize ITMS performance, the following six instrumental parameters were investigated in series: ''*q*'' value, resonance excitation voltage (REV), excitation time (ET), isolation time (IT), ion source temperature (IST) and electron energy (EE). The parameter ''*q*'' value is used in MS–MS and refers to the radio frequency (RF) voltage of constant frequency and variable amplitude that is applied to the ring electrode of the ion trap mass analyzer during CID of the precursor ion. Higher ''*q*'' values allow more energy to be deposited in the parent ion without ejecting it from the ion trap. For compounds that are hard to fragment because of their stability, a higher ''*q*'' value must be selected. REV, also known as collision energy, refers to the RF voltage applied to the endcap electrodes of the ion trap mass analyzer in MS–MS to cause the production of product ions from precursor ions through CID. When resonance excitation RF voltage is applied, it enhances the motion of selected ions in the axial direction to impart kinetic energy to them and thereby excite them. When ions are excited, collisions with the helium damping gas in the ion trap become more energetic until these ions gain enough internal energy to dissociate into product ions. ET is the duration that the resonance excitation RF voltage will be applied to the endcap electrodes of the ion trap mass analyzer to affect the production of

product ions from an isolated precursor ion via CID with damping gas molecules. IT refers to the duration of the ion isolation waveform voltage, which is applied to the endcap electrodes during the isolation of the precursor ions into the ion trap. The effect of each parameter, as well as the operation and application of ITMS have been thoroughly described previously [36–38].

Six series of injections from a PCBs mixture were made in order to investigate the signal intensity of each PCB congener by varying each one of the six instrumental parameters, cited above. Initially, the operating parameters were adjusted at the default values and then were optimized one by one in the same order as they were mentioned above.

For each series of injections, the instrumental parameter under investigation was gradually increased and the peak area of the product ions for 22 congeners was integrated. In order to check that the signal intensity of each congener was due to parameter variation alone and not to other possible effects (e.g., accidental changes of injected volume) the method of internal standard was used for four of the parameters, namely excitation voltage, excitation time, isolation time and ''*q*'' value. The relative response of each congener was then calculated for each injection according to the following equation:

$$\mathrm{RR(X)} = \frac{M(\mathrm{I.S.})}{M(\mathrm{X})} \cdot \frac{S(\mathrm{X})}{S(\mathrm{I.S.})}$$

where RR(X) is the relative response of a congener X with respect to the internal standard I.S. M(I.S.) and S(I.S.) are, respectively, the amount and peak area of the internal standard, and M(X) and S(X) are the corresponding amount and peak area of congener X.

To warrant a stable response of the internal standard (PCB 116), at a whole sequence of injections, the instrumental parameters applied during its elution were kept constant. Conversely, the value of the parameter under investigation, which was applied during the elution of the 22 congeners, was gradually increased injection by injection. As the same solution was used for all the injections, the ratio M(I.S.)/M(X) was kept constant and therefore the variation of RR depended on the variation of the S(X)/S(I.S.) ratio. Thus, the variation of RR, during a sequence of injections, reflected the variation of S(X) (for which the parameter varied) in relation to S(I.S.) (for which the parameters were kept constant for the whole series of injections).

2.3. Sampling

Eleven air samples were collected: (1) from the ECPL background sampling station (five samples) at Finokalia (35° 19′ N, 25° 40′ E), a coastal remote site 70 km eastward of Heraclion (Island of Crete, Greece). (2) At Kolympari (two samples) (35° 54′ N, 23° 80′ E) a rural coastal site 35 km westward of Chania (Island of Crete, Greece). (3) At Aspvreten (four samples) (58° 58′ N, 17° 23′ E), a forested area, situated on the Baltic coast in a national park about 100 km south of Stockholm (Sweden). The sampling period lasted between April and August 1999.

Samples were collected with a high-volume air sampler located at a height of 10 m from the ground. Sampling duration was 24 h and sample volumes ranged from 1000 up to 1700 m^3. Air was drawn first through a glass fiber filter (GFF) in order to collect particles and then through a polyurethane foam (PUF) plug (length 8.0 cm, diameter 7.5 cm) to collect the vapor-phase PCBs. Preceding sampling, GFFs were heated at 450°C for 5 h. PUF plugs were boiled in water, rinsed with acetone and Soxhlet extracted twice for 24 h with *n*-hexane. PUF plugs were dried into a vacuum dessicator, placed in glass cylinders and sealed in glass jars.

2.4. Sample clean up and analysis

We used PCB 116 as internal and PCBs 54, 155 and 185 as surrogate standards. These congeners were absent or in trace amount (PCB 185) in the commercial mixture Aroclor 1242 [39,40] used from 1929 up to the 1970s. Since it has been reported that the distribution of PCB congeners in the atmosphere is very similar to the corresponding of Aroclor 1242 [21,41,42], we expect a negligible amount of congeners 116, 54, 155 and 185 also in the atmosphere. For the same reason, other native PCBs have already been chosen as surrogate and internal standards in a previous study [43]. The PUF and GFF samples were

analyzed separately and prior to the analysis, each PUF and GFF was spiked with known amounts (5–20 ng) of surrogate standards (PCBs 54, 155, 185) and then Soxhlet extracted with *n*-hexane for 24 h. The extract was concentrated to 4 ml by rotary evaporation and then to 1 ml under a gentle nitrogen stream at ambient temperature. The sample was then loaded onto a 1.5 g silica gel column (100–200 mesh; activated at 150°C for 3 h; 1.0 cm I.D.) and eluted with 12 ml of *n*-hexane (1.4 ml/min) under nitrogen pressure. The eluted fraction was reduced to 4 ml by rotary evaporation and treated twice with 2 ml of concentrated H_2SO_4. Subsequently, the *n*-hexane phase was loaded onto a disposable Pasteur pipette packed with the following components: 1 cm of dehydrated $NaSO_4$, 1 cm of H_2SO_4 impregnated silica, 1 cm of KOH impregnated silica and 1 cm of deactivated silica in series. PCBs were further eluted with 6 ml of *n*-hexane. The extract was reduced by rotary evaporation to 0.5 ml, transferred into a 1 ml vial and further evaporated to dryness under a gentle nitrogen stream. Then, a known amount of internal standard PCB 116 (20 μl) was added and 2 μl of the sample were injected to the GC–ITMS system operating in MS–MS mode. The GC system was operated under the same conditions as those reported for the ITMS optimization. The six instrumental parameters were adjusted at the optimum values (Table 2) while the default values were set for all the other parameters.

The identification of the 23 PCBs (as reported in Section 2.1) in air samples was based on the chromatographic relative retention time (RRT) and the MS–MS spectrum obtained by injecting mixtures of pure PCB congeners. For the identification of other PCB congeners determined in this study, the MS–MS spectrum of the reference standards conjointly with the RRT values reported from Mullin et al. [44] were used. As a chromatographic column with the same kind of stationary phase and a similar oven temperature program, to those reported by Mullin et al. [44], were used the same RRT values should be expected. By correlating the retention times of the 23 PCBs analyzed in our study, with their corresponding RRT values obtained by Mullin et al. [44], an equation was derived. By using this equation and the obtained RRT values we estimated the retention time of other PCB congeners with a acceptable margin of ±5 s. Injecting several Aroclor mixtures validated this estimation method.

Relative response factors (RRFs) of all PCB congener were determined each time prior to sample analysis and were used to calculate the amount of each congener present in the samples. Since the calculation of RRF values was not possible for all congeners detected in air samples, RRF values derived by injecting the standard mixture of the 23 PCBs were used. The RRF of a congener, not contained in this mixture, was considered to be equal to the average RRF value calculated from its close eluting congeners in the standard mixture and with the same degree of chlorination.

2.5. Quality control and assurance

Two pre-cleaned PUF and two GFFs were used as field blanks and procedural blanks. Blanks were prepared, treated and analyzed as the samples. Blank values for individual PCB congeners were very low at both GFF and PUF samples and in most cases not detectable. The average total amount of PCBs under investigation was 1800 and 1010 pg for PUF and GFF, respectively. These amounts, for an aerosol sample of 1500 m^3, correspond to a concentration of 1.1 pg/m^3 for gas phase PCBs and 0.86 pg/m^3 for particulate phase PCBs, respectively.

A chromatographic peak was quantified as PCB, when the following criteria were met: (a) the S/N ratio should be higher than 5, (b) the isotope ratios for the two monitored product ions should be within ±15% of those observed for reference standards (Table 1), and (c) the retention time should be within the margin of ±2 s of those observed for reference standards. Congeners for which reference standards were not available, were identified as PCBs if criteria a and b were satisfied and if their retention times were within ±5 s of those estimated by their RRT values in [44], as described above.

3. Results and discussion

3.1. ITMS optimization

The precursor ion of each congener, chosen from its full scan mass spectrum, and its product ions,

Table 1
Precursor ions, the optimum range of product ions recorded for MS–MS, characteristic product ions and their corresponding ratios for each homologue group of PCBs

PCB homologue group	Precursor ion (m/z)	Optimum range of product ions (m/z)	Characteristic product ions (m/z)	Intensity ratio
Tri-CBs	256	186 to 188	186+188	100/1.8
Tetra-CBs	292	220 to 224	222+220	100/78.4
Penta-CBs	326	254 to 258	256+254	100/63.4
Hexa-CBs	360	288 to 292	290+288	100/54.1
Hepta-CBs	394	322 to 326	324+326	100/35.4
Octa-CBs	430	358 to 362	360+358	100/58.5

CB: Chlorinated biphenyl.

selected from the corresponding MS–MS mass spectrum, were the ions with the highest relative abundance in the appropriate mass spectrum. As expected, the congeners of the same degree of chlorination (homologue group) gave a similar full scan and MS–MS mass spectrum. This similarity characterizing the mass spectral fragmentation patterns of PCBs, with the same number of chlorine atoms, has been previously reported for electron [28], NCI mode [28,30] and as well as for ion trap MS–MS mode [45]. Even if differences at the relative abundance of ions $[M]^+$, $[M-Cl]^+$ and $[M-2Cl]^+$ were observed, for isomers having different number of *ortho*-chlorine atoms, the $[M]^+$ and the $[M-2Cl]^+$ ions were always the predominant ions in full scan and MS–MS mass spectra, respectively. Consequently, the same precursor and product ions were selected for the identification and quantification of all PCBs belonging to the same homologue group. The characteristic precursor and product ions for each PCB category are shown in Table 1.

Since the molecular ion $[M]^+$ dominated all other precursor ions produced during the electron ionization (e.g., $[M-Cl]^+$ and $[M-2Cl]^+$), the full scan mass spectra of PCBs may be characterized as non-dissociative according to Rothweiler and Berset [30]. The energy of electrons, during their impaction onto PCB molecules, was not high enough to induce quantitative dissociation of one or two chlorine atoms. Conversely, the second step (CID) was dissociative and the predominant product ion $[M-2Cl]^+$, indicates loss of two chlorine atoms from the corresponding precursor ion. The quantitative dissociation of two chlorine atoms indicated that CID is a more intensive process than EI. The dissociative character of CID, when an ion trap mass spectrometer is used, has also been previously reported for the congeners PCB 77 (tetrachlorobiphenyl) and PCB 169 (hexachlorobiphenyl) [35].

As the improvement of ITMS specificity to PCBs was among the targets of this study the mass range of the product ions, to be acquired and recorded for each PCB homologue group, was narrowed in order to avoid potential interferences from non-PCB ions. The appropriate ranges of product ions for each homologue group are also presented in Table 1. Characteristic mass spectra, obtained for tetra- and penta-CBs are illustrated in Fig. 2.

The ITMS parameters were varied in order to determine the suitable values at, which the absolute peak area of the product ions and their relative response (RR) were optimal for the congeners under investigation. The results of this experiment are visualized, for the six PCB homologue groups, in Fig. 3a–f. All congeners belonging at the same homologue group showed a similar behavior during the variation of a parameter and therefore only the average peak areas (APAs) were plotted. For isolation time, excitation time, resonance excitation voltage and ''q'' value the graphs of the average RR against each parameter were also plotted for each homologue group of PCBs. These graphs are not provided since they had almost the same variation patterns as those of APAs. The similarity of both graphs indicated that accidental changes of the injected volume were insignificant and did not affect the results of the optimization experiment.

The plot of isolation time (IT) (Fig. 3a) shows that the APAs of all PCBs were not substantially affected by the variation of this parameter.

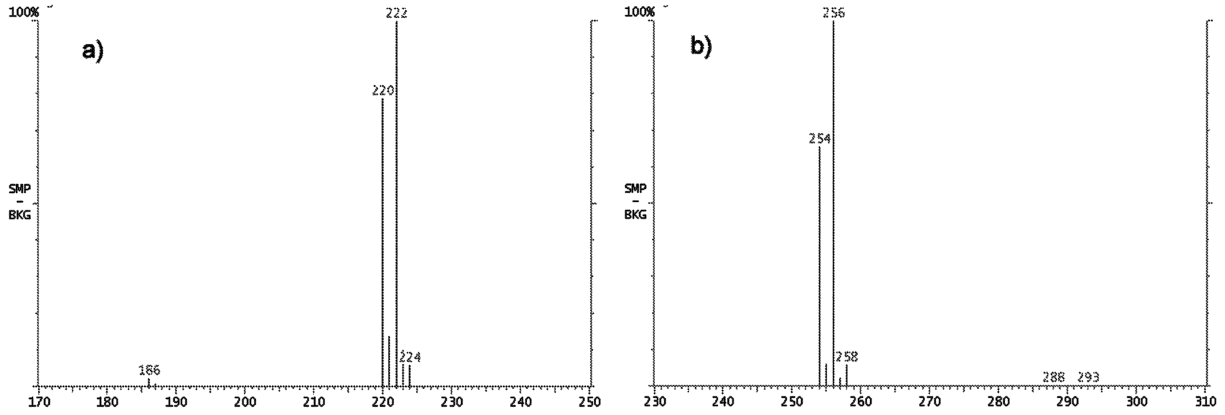

Fig. 2. Characteristic MS–MS mass spectra, obtained for (a) tetra-CBs and (b) penta-CBs.

The variation patterns of excitation time (ET) (Fig. 3b) and relative excitation voltage (REV) (Fig. 3c) were very similar. Low values for these parameters resulted in a decrease on PCBs APA, while no signal was observed when the ET and REV approached 1 ms and 0.5 V, respectively. A maximum for the PCBs APA occurred when REV was 2 V and when ET varied between 5 and 15 ms. At higher values for both parameters, the same or even lower APAs of PCBs congeners were observed.

Only three values (instrument characteristics) can be set for ''*q*''. An important increase of APA was observed for all PCB congeners when ''*q*'' value increased from 0.225 to 0.3 (Fig. 3d). Also, all congeners from trichlorobiphenyls (tri-CBs) up to heptachlorobiphenyls (hepta-CBs) have shown a continuous APA increase when ''*q*'' values increased from 0.3 up to 0.45. However, this increase has been more remarkable for the tri-CB (increase of 168%) up to pentachlobiphenyl (penta-CB) (increase of 57%) congeners (Fig. 3d). The corresponding increase for the congeners with higher chlorination degree (e.g., hepta-CB) was only 26%. Only the octachlorobiphenyl (octa-CB) congeners showed a maximum APA when ''*q*'' equaled 0.3 (Fig. 3d). Since higher ''*q*'' values allow more energy to be deposited in the precursor ion before its dissociation (CID), we concluded that octa-CBs needed to be excited at lower energy before the dissociation of two chlorine atoms takes place. This is reasonable if we consider that a chlorine atom can be removed more easily from a biphenyl ''crowded'' with eight chlorine atoms than a biphenyl having fewer chlorine atoms.

The electron energy (EE) and the ion source temperature (IST) can substantially affect the sensitivity of ITMS, as an increase of these two parameters results to a significant increase in the APA of PCB congeners (Fig. 3e and f). It must be noted that APA increased exponentially with the IST and almost linearly with the EE (Fig. 3e and f). The APA of tri- and octa-CBs increased by 630% and 1070%, respectively when IST increased from 130 to 210°C. In addition, when EE increased from 35 to 80 eV, the APA of all homologue groups increased approximately by 110%.

Except for isolation time, all the other parameters had a substantial effect on the MS–MS determination of PCBs and thus their adjustment was crucial. The optimum conditions for the determination of PCBs by ion trap MS–MS, extracted from this experiment, are summarized in Table 2.

The obtained optimum conditions for the instrumental parameters (Table 2) were used to check the sensitivity and linearity of ITMS. For this purpose a series of standard solutions, containing 22 PCB congeners with concentrations varying between from 0.6 up to 300 pg/μl, were analyzed. Due to the absence of background signals, high signal-to-noise (S/N) ratios were obtained even for the solution with the lowest concentration of 600 fg/μl (Table 3). Although, high enough S/N were also obtained at lower concentration (e.g., 400 fg/μl), the resulting chromatographic peak shapes or the mass spectra for

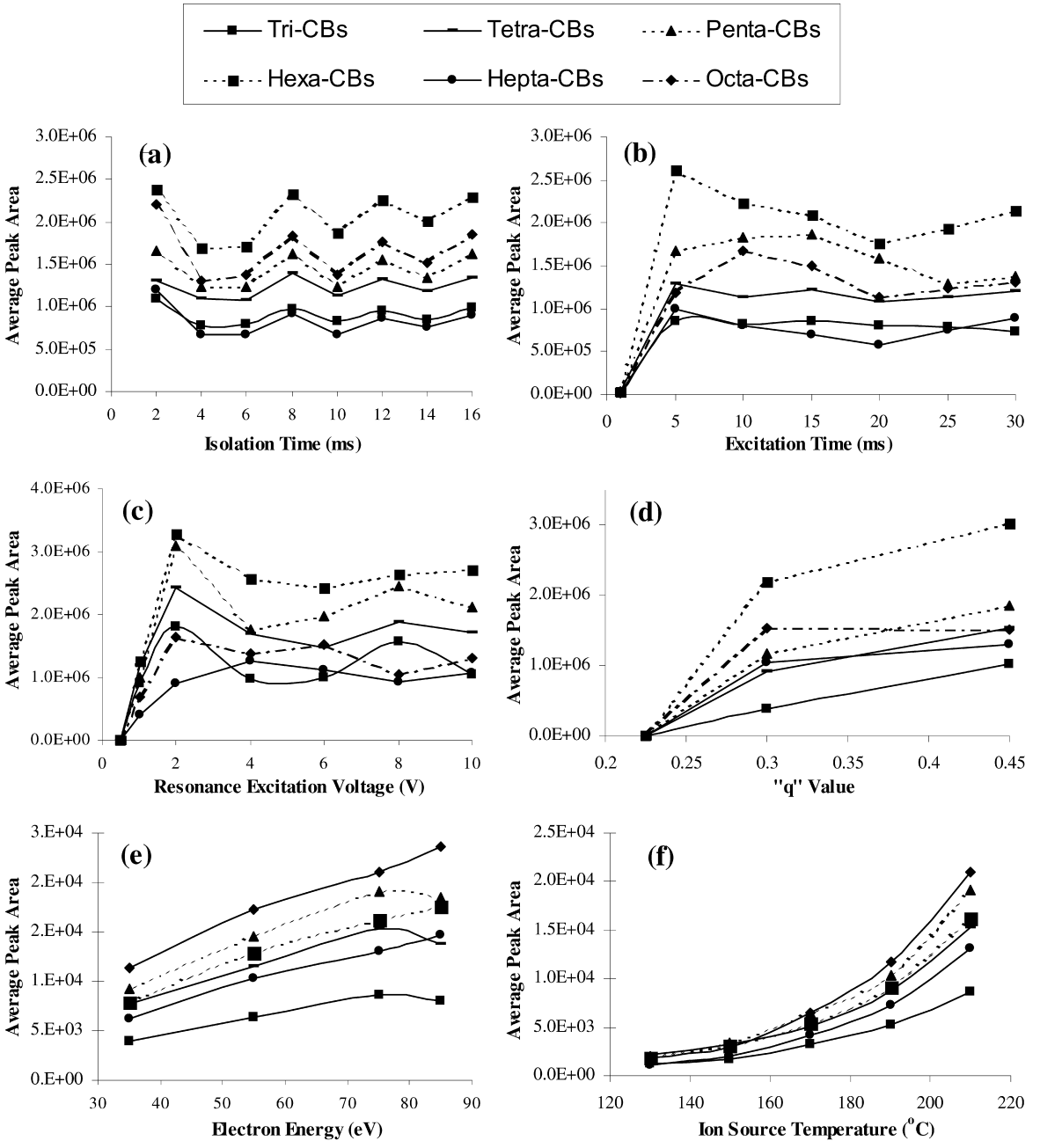

Fig. 3. Plots of average peak area (APA) versus isolation time (IT), excitation time (ET), resonance excitation voltage (REV), ''q'' value, electron energy (EE) and ion source temperature (IST) for the six homologue PCB groups.

some congeners were poor and therefore not suitable for a reliable integration. We noticed that the penta-CB congeners 90, 101, 110, 123, 105 and the octa-CB congener 194 have shown the lowest S/N ratios (8–12 and 11, respectively; Table 3). On the contrary the tetra-CB congener 70 and the octa-CB congeners 155, 153 demonstrated the highest S/N ratios (87 and 91, respectively; Table 3). Penta-CB

Table 2
Optimum parameter values for the determination of PCB congeners by ion trap MS–MS technique

PCB category	"q" Value	Excitation time (ms)	Excitation voltage (V)	Isolation time (ms)	Electron energy (eV)	Ion source temperature (°C)
Tri-CBs	0.45	5	2	2	70	210
Tetra-CBs	0.45	5	2	2	70	210
Penta-CBs	0.45	10	2	2	70	210
Hexa-CBs	0.45	5	2	2	70	210
Hepta-CBs	0.45	5	2	2	70	210
Octa-CBs	0.3	10	2	2	70	210

congeners produced some ions similar to those corresponding to capillary column bleeding and for this reason the baseline noise was higher.

Linearity of the ITMS detector response is a parameter of utmost importance for quantification purposes. We studied this parameter by constructing a six-point calibration curve with standard solutions covering concentrations from 0.6 to 300 pg/μl. In these solutions, the concentration of the internal standard was kept constant (200 pg/μl). We performed the injections by decreasing gradually the concentration of the congeners under investigation.

Table 3
Signal-to-noise (S/N) ratios, average recovery of the analytical method (GFF and PUF, spiked with 22 congeners representative for all homologue groups) and method detection limit

PCB congener	S/N for 600 fg/μl	Average recovery (%)	Method detection limit (fg/m^3)
18	65	51.3	17
28	58	83.8	11
54	83	74.5	12
52	78	75.9	12
70	87	81.3	11
90+101	8	67.9	13
110	10	67.1	13
123	12	85.1	10
118	20	77.9	11
105	12	87.6	10
155	91	49.7	18
149	72	77.0	11
132	55	73.6	12
153	91	82.2	11
138	65	78.5	11
158+160	85	78.2	11
185	36	88.7	10
180	72	98.2	9
199	22	85.0	10
194	11	98.2	9

Moreover the range of concentrations we used, was sufficiently representative for the determination of PCBs in the suspended particles of the atmosphere. The logarithm of relative amount [$\log(M_X/M_{PCB\ 116})$] of each congener (M_X) to the corresponding amount of the internal standard ($M_{PCB\ 116}$) has been plotted versus the logarithm of its corresponding relative peak area [$\log(S_X/S_{PCB\ 116})$]. Logarithimic scale was used since the concentrations of standard solutions covered four orders of magnitude. The quality of calibration was assessed by calculation of correlation coefficient (R^2) of the linear calibration curves. Representative calibration curves for the tri-CB congener 18 (representing the less chlorinated congeners) and the octa-BC congeners 194 (representing the congeners with highest degree of chlorination) are shown in Fig. 4. The R^2 values obtained varied between 0.971 and 0.997. The average R^2 for the 22 congeners was 0.990 and can be considered as very satisfactory for the purpose of this study.

3.2. Analytical performance

The recovery of an overall analytical technique, which is used for the quantitation of micro-pollutants like PCBs, must be sufficiently high. In order to check the recovery of the method (including all steps from extraction, through clean-up, to GC–ITMS analysis) developed in this study, two pre-cleaned PUFs and two GFFs were spiked with 5 ng of each PCB congener and were then treated as real samples. The average recoveries are shown in Table 3. Most of the congeners have shown high recoveries ranging between 68 and 98% (Table 3). Only PCB congeners 54 and 155 gave recoveries between 50 and 51% (Table 3). In order to check possible losses of major

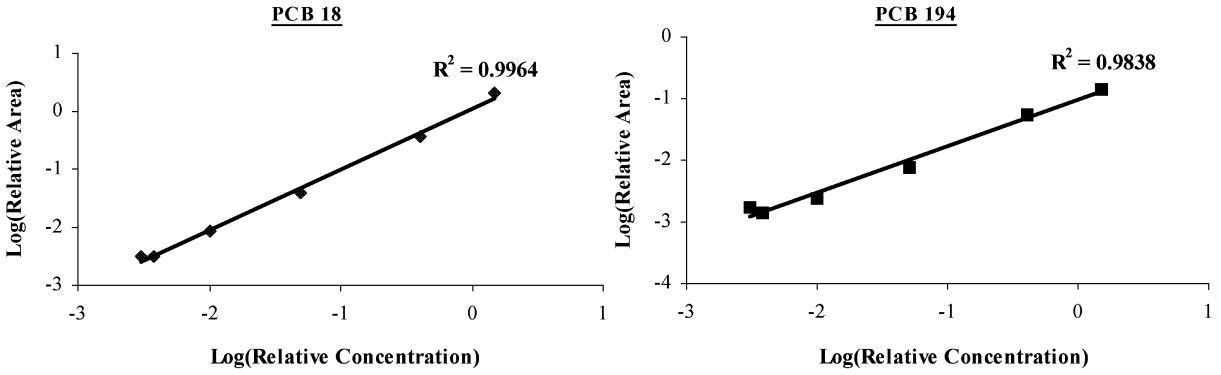

Fig. 4. Plots of the logarithm of relative concentration versus the logarithm of relative peak area for the PCB congeners 18 and 194.

PCB amounts, throughout the whole analytical procedure, we checked each one of the steps of the analytical method. We found that the major PCBs loss was occurring during the solvent evaporation step with nitrogen stream. This is in accordance with a previous study concerning other POPs [46]. The recovery during the analysis of these four samples showed a relative standard deviation ranging between 8.0% (PCB 155) and 32.3% (PCB 54) with an average value for all congeners approximating 18.4% (Table 3).

By considering the instrumental detection limit for PCBs (600 fg/μl) and the average volume of an air sample (1350 m^3) we calculated, by using the recovery of the method, the approximate method detection limit for each PCB congener (Table 3). The high sensitivity and specificity, obtained in this study for the ion trap MS–MS technique, the high recovery of the whole analytical method and the use of a high volume sampler makes feasible the quantitation of atmospheric PCBs at the low pg or fg/m^3 level (9–18 fg/m^3; Table 3). Fig. 5 (congener numbers are given according to Ballschmiter and Zell [47]) shows the MS–MS chromatogram (divided to a different section for each homologue group) of an extract of a background marine aerosol collected at Finokalia. We can observe that even for a very low total PCB amount (<30 pg/m^3), individual congeners can be reliably identified and quantified.

3.3. Determination of PCBs in marine and rural background aerosols

PUF plugs (containing the aerosol gas phase) were analyzed separately from GFF filters (containing the aerosol particulate phase). As mentioned above, characteristic ion chromatograms of six homologue PCB groups, from a sample (PUF plug) extract collected at Finokalia, are shown in Fig. 5. More PCB congeners than those contained in our standard solution, were identified as described above (see Section 2.5).

Mean concentrations of total PCBs and a subset of ca. 35 congeners, determined separately in the gas and the particulate phase of aerosol samples collected in Kolympari and Finokalia (Island of Crete, Greece) and Aspvreten (Sweden) are listed in Table 4.

Mean total PCB concentrations for the sampling period were 91.80 pg/m^3 (90.38 pg/m^3 for the gas and 1.42 pg/m^3 for the particulate phase, respectively) for Kolympari, 33.61 pg/m^3 (31.15 pg/m^3 for the gas and 2.46 pg/m^3 for the particulate phase, respectively) for Finokalia and 35.30 pg/m^3 (34.26 pg/m^3 for the gas and 0.94 pg/m^3 for the particulate phase, respectively) for Aspvreten. Fig. 6 shows the percentage of the mean total PCB concentration, each homologue group represents in the sampling period at the three sites. In Kolympari tri-CBs and tetra-CBs (over 60%; Fig. 6) dominated the other homologue congener groups. The lighter tri-CBs were the most predominant (over 50% in Finokalia and over 40% in Aspvreten; Fig. 6) in comparison to tetra-CB through octa-CB congeners. The homologue profiles presented in Fig. 6 tend to show uniformity regardless of the site (e.g., Finokalia and Aspvreten), with a decreasing contribution with increasing chlorination.

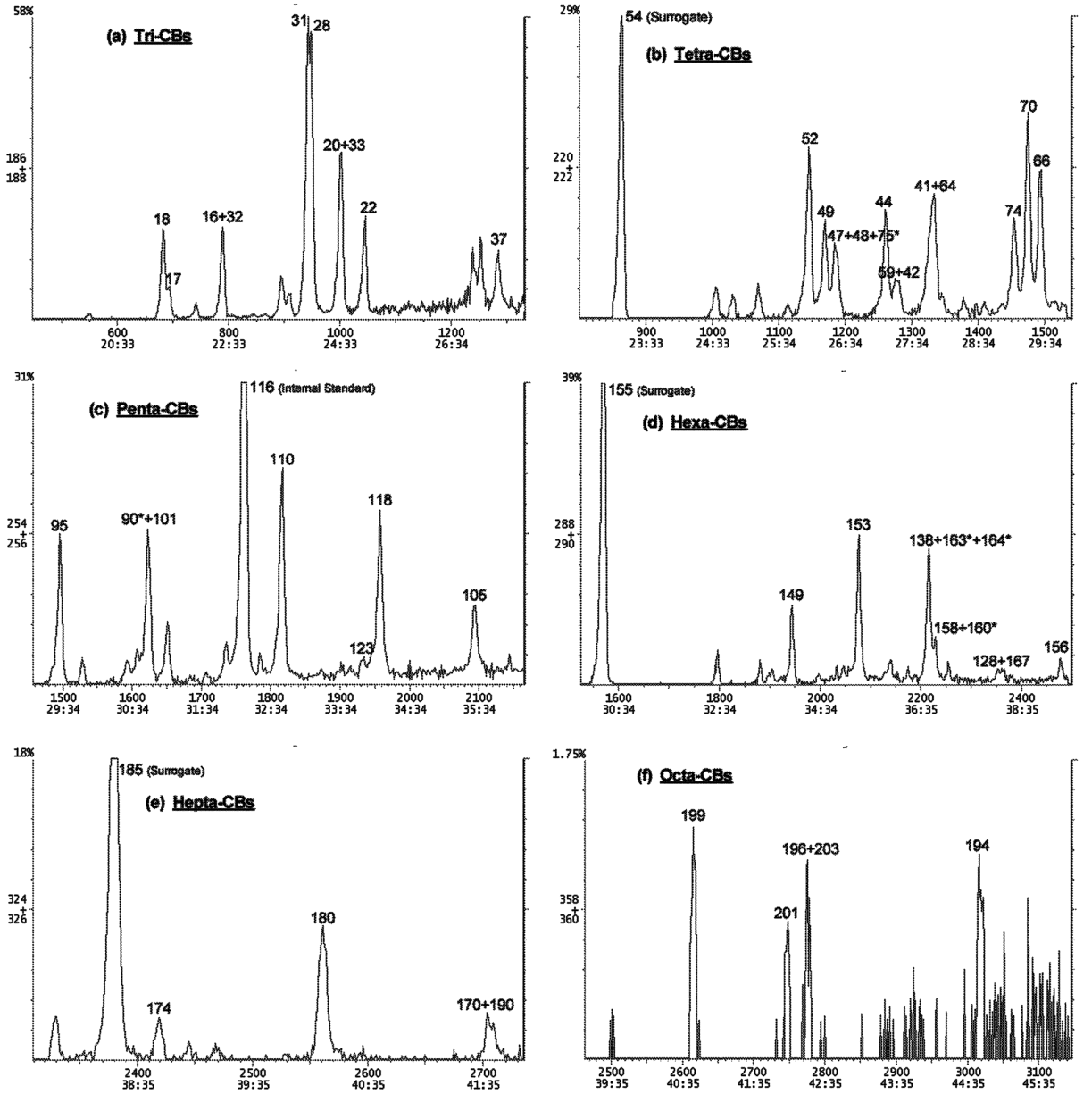

Fig. 5. MS–MS chromatogram (for ions see Table 1) of a marine aerosol sample collected at Finokalia. The chromatogram is divided into segments corresponding to each PCB homologue group. The individual congeners are numbered according to Ballschmiter and Zell [47]. *Indicates the congeners supposed to have low or very low concentration relatively with other coeluting isomers according to Refs. [39,40].

Mean total PCB concentration measured in Kolympari (Table 4), a rural site, is lower than the concentrations measured in other rural sites in the UK (46–471 pg/m^3; [48]) and the USA (128–480 pg/m^3; [49]). The mean concentration (Table 4) for the background marine station of Finokalia is in the same order of magnitude to the concentrations observed in Arctic background stations such as Alert (27.4 pg/m^3), Tagish (17.0 pg/m^3) and Dunai (34.0 pg/m^3) [49]. Finokalia total PCB mean concentration is also similar to this measured in the air of Lake Baikal region in Russia (8.7–23 pg/m^3; [50]).

Table 4
Individual congener and total PCB concentration in the gas and particulate phase in background aerosol samples collected at Kolympari and Finokalia (Island of Crete, Greece) and Aspvreten (Sweden)

PCB Congener	Kolympari ($N=2$)		Finokalia ($N=5$)		Aspreveten ($N=4$)	
	Vapor (pg/m^3)	Particles (pg/m^3)	Vapor (pg/m^3)	Particles (pg/m^3)	Vapor (pg/m^3)	Particles (pg/m^3)
18	4.42 (±2.83	n.d.	2.92 (±2.35)	0.182 (±0.102)	4.89 (±1.84)	0.087 (±0.041)
17	2.21 (±0.94)	n.d.	1.51 (±0.36)	0.098 (±0.051)	0.94 (±0.19)	0.023 (±0.012)
16+32	4.12 (±1.62)	n.d.	1.88 (±0.23)	0.177 (±0.076)	2.02 (±0.87)	0.051 (±0.030)
31	9.88 (±1.93)	0.094 (±0.132)	5.30 (±1.00)	0.575 (±0.277)	3.68 (±1.47)	0.117 (±0.047)
28	8.09 (±1.58)	0.077 (±0.108)	4.54 (±1.15)	0.481 (±0.160)	3.01 (±1.21)	0.095 (±0.039)
53	0.67 (±0.20)	n.d.	0.31 (±0.05)	n.d.	0.50 (±0.29)	n.d.
52	13.35 (±1.07)	0.047 (±0.066)	2.43 (±0.45)	0.096 (±0.104)	1.93 (±1.18)	0.023 (±0.006)
49	5.61 (±0.41)	n.d.	1.48 (±0.22)	0.068 (±0.083)	0.88 (±0.56)	n.d.
47+48+75*	1.71 (±2.36)	n.d.	1.20 (±0.22)	0.038 (±0.035)	1.07 (±1.00)	0.011 (±0.013)
44	7.72 (±0.46)	n.d.	1.39 (±0.28)	0.064 (±0.075)	0.84 (±0.45)	0.017 (±0.023)
74	1.19 (±0.05)	0.003 (±0.005)	0.83 (±0.28)	0.066 (±0.078)	0.65 (±0.40)	0.019 (±0.017)
70	2.68 (±0.07)	0.019 (±0.028)	1.31 (±0.54)	0.118 (±0.069)	1.76 (±1.22)	0.050 (±0.018)
66	0.64 (±0.73)	0.095 (±0.103)	0.98 (±0.32)	0.150 (±0.091)	0.88 (±0.49)	0.024 (±0.010)
95	1.53 (±0.19)	0.045 (±0.019)	0.58 (±0.38)	0.042 (±0.050)	0.95 (±0.43)	n.d.
101+90*	0.98 (±0.37)	0.005 (±0.007)	0.74 (±0.81)	0.032 (±0.047)	1.60 (±0.85)	0.025 (±0.017)
99	0.62 (±0.16)	n.d.	0.18 (±0.14)	n.d.	0.30 (±0.17)	n.d.
110	1.57 (±0.31)	0.008 (±0.011)	0.67 (±0.24)	0.034 (±0.051)	1.34 (±0.72)	0.039 (±0.013)
123	0.03 (±0.02)	0.003 (±0.004)	0.04 (±0.01)	n.d.	0.04 (±0.02)	n.d.
149	0.70 (±0.15)	n.d.	0.56 (±0.42)	0.031 (±0.032)	1.67 (±0.57)	0.047 (±0.010)
118	1.18 (±0.21)	0.016 (±0.023)	0.36 (±0.28)	0.024 (±0.037)	1.08 (±0.55)	0.057 (±0.022)
153	12.91 (±0.31)	0.371 (±0.524)	0.77 (±0.18)	0.044 (±0.031)	2.05 (±0.62)	0.081 (±0.013)
132	n.d.	n.d.	0.13 (±0.24)	0.023 (±0.025)	0.43 (±0.38)	0.016 (±0.012)
105	2.72 (±0.54)	0.146 (±0.206)	0.20 (±0.06)	n.d.	0.36 (±0.16)	0.045 (±0.055)
138+164*+163*	4.55 (±0.28)	0.262 (±0.370)	0.39 (±0.18)	0.027 (±0.009)	0.66 (±0.18)	0.031 (±0.003)
158+160*	0.60 (±0.09)	0.148 (±0.209)	0.14 (±0.15)	0.030 (±0.018)	0.38 (±0.08)	0.023 (±0.013)
180	0.69 (±0.07)	0.086 (±0.121)	0.25 (±0.04)	0.017 (±0.014)	0.30 (±0.10)	0.040 (±0.008)
199	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
194	n.d.	n.d.	0.04 (±0.03)	n.d.	0.03 (±0.02)	n.d.
Total PCBs	90.38	1.424	31.15	2.455	34.26	0.943

The number of samples is given in parentheses. *Indicates the PCBs congeners that should slightly contribute on the peak of two or three coeluting isomer PCBs according to Refs. [39,40]. n.d. is assigned for PCBs having concentration lower than the method detection limit.

Conversely, the mean PCB concentration reported here, for Finokalia, is lower than the corresponding observed in Bermuda (380 pg pg/m^3), where 80 congeners were measured [21]. PCB mean concentration (Table 4) determined in Aspvreten, considered as a background station for the Stockholm metropolitan area, was lower or in the same order of magnitude than the corresponding concentrations found in some UK rural areas such as Chilton and Wraymires [51].

4. Conclusions

In this study the optimization of an ion trap MS–MS technique for PCBs was carried out. The optimum values for six instrumental parameters, including isolation time, excitation voltage, excitation time, ''*q*'' value, ion source temperature and electron energy were obtained, in order to enhance the MS sensitivity. The adjustment of almost all the parameters proved crucial for the ITMS sensitivity, but the significance of ion source temperature was particularly noted. The linearity of ITMS using the internal standard method was good for all PCB congeners with concentrations ranging between 0.6 and 300 pg/μl. The sensitivity was also sufficient, even for injections of 600 fg/μl, since the S/N ratios ranged between 10 and 90.

GC–ITMS, operating in the MS–MS mode, was

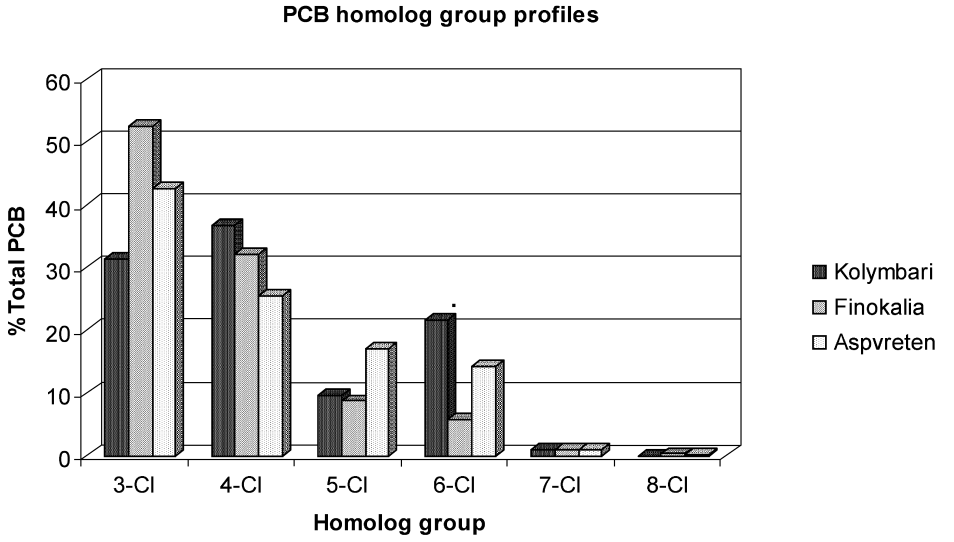

Fig. 6. PCB homologue group patterns (% total PCBs) for background aerosol collected at Kolympari and Finokalia (Island of Crete, Greece) and Aspvreten (Sweden) sampling sites.

used for the quantitation of PCBs in the gas phase and the suspended particles in the atmosphere of three background sites. The high selectivity and the high sensitivity of the ion trap MS–MS technique was sufficient for the determination of PCBs even at the particulate phase where the concentrations of most PCBs were in the range of 100 fg/m^3. The concentrations determined in this study are in accordance with other studies, where the predominance of vapor phase PCBs over the particulate ones was observed. The concentrations determined in the Eastern Mediterranean can be considered among the lowest observed all over the world. Our results are the first, to our best knowledge, to be presented for background aerosol PCBs concentration in the Mediterranean basin.

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References

[1] B.D. Rodan, D.W. Pennington, N. Eckley, R.S. Boethling, Environ. Sci. Technol. 33 (1999) 3482.
[2] F. Wania, D. Mackay, Ambio 22 (1993) 10.
[3] H. Iwata, S. Tanabe, N. Sakai, R. Tatukawa, Environ. Sci. Technol. 27 (1993) 1080.
[4] J.D. Jeremiason, K.C. Hornbuckle, S.J. Eisenreich, Environ. Sci. Technol. 28 (1994) 903.
[5] S. Datta, L. McConnell, J. Baker, J. Lanoir, J. Seiber, Environ. Sci. Technol. 32 (1998) 1378.
[6] N. Kannan, N. Yamashita, G. Petrick, J. Duinker, Environ. Sci. Technol. 32 (1998) 1747.
[7] B. Gevao, J. Hamilton-Taylor, K.C. Jones, Environ. Pollut. 102 (1998) 63.
[8] I. Cousins, B. Gevao, K.C. Jones, Chemosphere 39 (1999) 2507.
[9] T. Harner, D. Mackay, K.C. Jones, Environ. Sci. Technol. 29 (1995) 1200.
[10] R.E. Alcock, A.E. Johnston, S.P. McGrath, M.L. Berrow, K.C. Jones, Environ. Sci. Technol. 27 (1993) 1918.
[11] R. Fuoco, M.P. Colombini, C. Abete, Int. J. Environ. Anal. Chem. 55 (1994) 15.
[12] D. Broman, C. Naf, J. Axelman, H. Pettersen, Chemosphere 29 (1994) 1325.
[13] E. Brorstrom-Lunden, C. Lofgren, Environ. Pollut. 102 (1998) 139.

[14] K.C. Jones, G. Sanders, S.R. Wild, V. Burnett, A.E. Johnston, Nature 356 (1992) 137.
[15] J.P. Villeneuve, E. Fogelqvist, C. Cattini, Chemosphere 17 (1988) 399.
[16] L. Marsili, M.C. Fossi, G. Notarbartolo Di Sciara, M. Zanardelli, B. Nani, S. Panigada, S. Focardi, Chemosphere 37 (1998) 1501.
[17] A. Borrell, A. Aguilar, T. Pastor, Mar. Pollut. Bull. 34 (1997) 505.
[18] S. Safe, CRC Crit. Rev. Toxicol. 13 (1984) 319.
[19] P. Coleman, R. Lee, R. Alcock, K.C. Jones, Environ. Sci. Technol. 31 (1997) 2120.
[20] E. Atlas, C.S. Giam, Science 211 (1981) 163.
[21] S.Y. Panshin, R.A. Hites, Environ. Sci. Technol. 28 (1994) 2001.
[22] D.J. Gregor, W.D. Gummer, Environ. Sci. Technol. 23 (1989) 561.
[23] K.C. Jones, V. Burnett, R. Duarte-Davidson, K.S. Waterhouse, Chem. Br. 27 (1991) 435.
[24] S.J. Harrad, A.S. Stewart, R. Boumphrey, R. Duarte-Davidson, K.C. Jones, Chemosphere 24 (1992) 1147.
[25] J.W. Cochran, G.M. Frame, J. Chromatogr. A 843 (1999) 323.
[26] E. Storr-Hansen, J. Chromatogr. 558 (1991) 375.
[27] M.D. Erickson, in: Analytical Chemistry of PCBS, 2nd ed., Lewis, New York, 1997, p. 235.
[28] H. Bagheri, P.E.G. Leonards, R.T. Ghijsen, U.A.Th. Brinkman, Int. J. Environ. Anal. Chem. 50 (1993) 257.
[29] R. Chaler, R. Vilanova, M. Santiago-Silva, P. Fernandez, J.O. Grimalt, J. Chromatogr. A 823 (1998) 73.
[30] B. Rothweiler, J.D. Berset, Chemosphere 38 (1999) 1517.
[31] J. Ferrario, C. Byrne, A.E. Dupuy, Chemosphere 34 (1997) 2451.
[32] P.R. Gardinali, T.L. Wade, L. Chambers, J.M. Brooks, Chemosphere 32 (1996) 1.
[33] Th. Kuchler, H. Brzezinski, Chemosphere 40 (2000) 213.
[34] D.G. Hayward, Chemosphere 34 (1997) 929.
[35] P.E.G. Leonards, U.A.Th. Brinkman, W.P. Cofino, Chemosphere 32 (1996) 2381.
[36] R. Heather, in: GCQ MS Detector Operator's and Service Manual, Technical Publications, Finnigan MAT, San Jose, CA, 1995, p. 1.1.
[37] R.E. March, J. Mass Spectrom. 32 (1997) 351.
[38] E.D. Hoffmann, J. Mass Spectrom. 31 (1996) 129.
[39] D.E. Schultz, G. Petrick, J.C. Duinker, Environ. Sci. Technol. 23 (1989) 852.
[40] G.M. Frame, Fresenius J. Anal. Chem. 357 (1997) 714.
[41] M. Hermanson, R. Hites, Environ. Sci. Technol. 23 (1989) 1253.
[42] J.B. Manchester-Neesviga, A.W. Andren, Environ. Sci. Technol. 23 (1989) 1138.
[43] S. Ayris, G.M. Currado, D. Smith, S. Harrad, Chemosphere 35 (1997) 905.
[44] M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Safe, L.M. Safe, Environ. Sci. Technol. 18 (1984) 468.
[45] J.W. Cochran, in: Proceedings of the 19th International Symposium on Capillary Chromatography, Wintergreen, VA, 1997, p. 250.
[46] K.J. Bombaugh, W.J. Cooper, W. Giger, K. Grob, J.R. Hass, F.K. Kawahara, J.A. Leenheer, D.L. Norwood, R.P. Schwarzenbach, J.C. Young, in: R.A. Minear, L.H. Keith (Eds.), Water Analysis, Organic Species, Vol. III, Academic Press, 1984, p. 117, Chapter 3.
[47] K. Ballschmiter, M. Zell, Fresenius J. Anal. Chem. 302 (1980) 20.
[48] G.M. Currado, S. Harrad, Environ. Sci. Technol. 34 (2000) 78.
[49] G.A. Stern, C.J. Halsall, L.A. Barrie, D.C.G. Muir, P. Fellin, B. Rosenberg, F.Ya. Rovinsky, E.Ya. Kononov, B. Pastuhov, Environ. Sci. Technol. 31 (1997) 3619.
[50] H. Iwata, S. Tanabe, K. Ueda, R. Tatsukawa, Environ. Sci. Technol. 29 (1995) 792.
[51] K.C. Jones, R. Duarte-Davidson, P.A. Cawse, Environ. Sci. Technol. 29 (1995) 272.