Polychlorinated Biphenyl Compounds (PCBs) Determination from Water by Gas Chromatography Coupled with Mass Spectrometry (GC–MS)

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Because they are not biodegradable, PCBs contribute to irreversible environmental pollution, and by ingestion, accumulate in adipose tissue, contributing to endocrine disrupters. By reason of these problems, it is necessary to improve the sensitivity and speed of PCB monitoring technology. In general, PCB is analyzed by gas chromatography with electron capture detector (GC-ECD) using classical columns with packed or capillary columns. These conventional analytical techniques, however, have accuracy problems in PCB detection that can occur due to interference owing to the matrix. The detection method by mass spectrometry, in the variant Selected Ion Monitoring contributes to the elimination of some interference between PCBs and some chemical compounds from the matrix, remained after the separation step. It chased the development of an analytical method for PCBs determination in water matrix by gas chromatography on fussed capillary column coupled with quadrupole mass spectrometry. As the method has been developed in laboratory, the method validation has been necessary studying the following performance parameters: specificity, selectivity, repeatability, intermediary precision, recovery, detection limit and robustness. The development of GC-MS method for PCBs determination in water consisted in establishing of the separation conditions of the analyzed components from water matrix (at an adequate recovery), by liquid-liquid extraction, the establishing of the optimal GC-MS parameters and the validation of this method. In the step of the analytes-matrix separation, PCBs from water samples prepared for analysis was extracted with hexane, carbon disulfide and chloroform through stirring at an appropriate speed followed by separating funnel separation. The organic fractions were concentrated to a final volume of 10 mL at a constant vacuum, with a Kuderna-Denish evaporator for GC-MS analysis. In the step II were established the optimal GC-MS separation parameters. The detection and quantitative determination by mass spectrometry, in the variant Selected Ion Monitoring"(MS-SIR) was used. In order to determine the PCBs recovery of the samples, three series of standards of the PCBs 28, 52, 101, 138, 153, 180 of 10 ppb in the solution to be analyzed using as extraction solvent hexane, carbon disulfide and chloroform were used. Recovery levels obtained were between 50% and 117% for hexane, 37 - 127 % for carbon disulfide and 65-111 % for chloroform. The selectivity, determined as lack of interferences with the compounds of interest, was achieved through the repeatability of the gas chromatographic retention times and by quantification ion and qualifying ions from MS-SIR method. This improved selectivity eliminates interferences between PCBs and some chemical compounds in water matrix remaining after liquid-liquid extraction step and incomplete gas chromatographic separation.The GC-MS-SIR method performs an adequate separation of PCBs from the water matrix and eliminates some extractible interfering elements with a recovery of 50-120 % and determines the PCBs in the concentration range of 1-100 pg/mL PCB in water (1-100 ng/mL in the solution to be analyzed

Keywords: PCBs, environmental pollution, GC-MS

Polychlorinated biphenyls (PCBs) are a class of organic compounds widely used in industry until the hazard posed to both the environment and human health by their use became evident. Due to their toxicity, chronic persistence and bioaccumulation, they have been restricted, and some of them have been included in the list of priority pollutants in many countries. As residues of these contaminants are present in water, soils, sediments, etc., they can transfer from waters/soils to aquatic organisms such as plankton, algae, and fish and consequently to birds and marine mammals. Humans are ultimately exposed to these compounds primarily through the diet, mainly by consumption of fish, mollusks and dairy products [1].

Because they are not biodegradable, PCBs contribute to irreversible environmental pollution [2] being necessary to improve the sensitivity and speed of PCB monitoring technology.

In general, PCB is analyzed by gas chromatography with electron capture detector (GC-ECD) using classical columns with packed or capillary columns. These conventional analytical techniques, however, have accuracy problems in PCB detection that can occur due to interference owing to the matrix.

The detection method by mass spectrometry, in the variant *Selected Ion Monitoring* contributes to the elimination of some interference between PCBs and some chemical compounds from the matrix, remained after the separation step and not separated by gas chromatography [3,4].

The objective of this paper was the development of an analytical method for PCBs determination in water matrix by gas chromatography on fussed capillary column coupled with quadrupole mass spectrometry, which performs an adequate separation of PCBs from the water matrix and

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GAS CHROMATOGRAPH PARAMETERS	
Injection mode	splitless
Injection port temperature	300 °C
Injection volume	2 µl
GC-MS interface temperature	280 °C
Column: - stationary phase - size - temperature program	Elite-5MS (5% diphenyl methyl polysiloxane) 60 m x 0.32 mm x 0.25 µm film thickness of stationary phase 70 °C (2 min.), 17 °C/min, to 170 °C 4 °C/min, to 280 °C, 15 min
MASS-SPECTROMETER PARAMETERS	
Ion source temperature	250 °C
Energy electrons	70 eV
Acquisition mode	SIM (Selected Ion Monitoring)

Table 1
GC-MS METHOD AND OPTIMISATION PARAMETERS

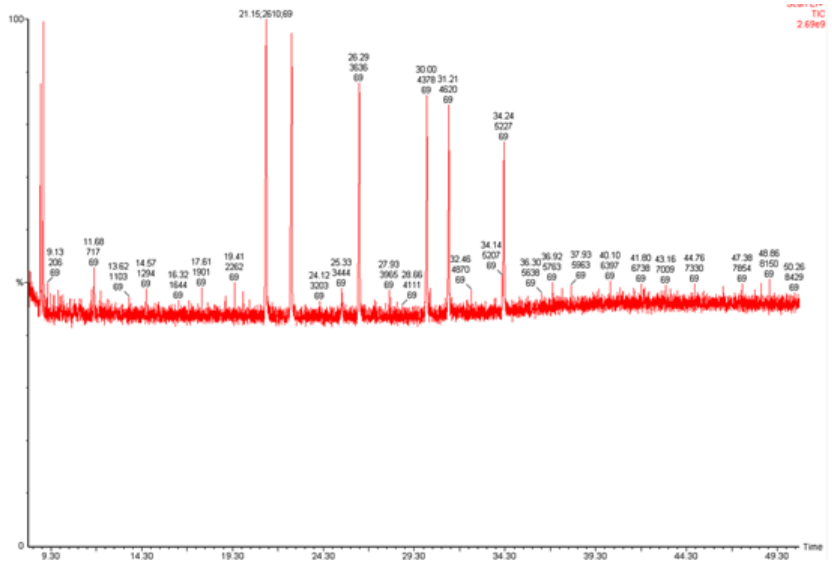

Fig.1. The chromatogram of a solution mixture of PCB28, PCB52, PCB101, PCB153, PCB138, PCB180 of 10 µg/mL

Group of PCBs	Retention time min.	PCB congener(s) measured	m/z (1)	m/z (2)	m/z (3)
Tri (Cl_3) PCBs	21.15	28	256	258	260
Tetra (Cl_4) PCBs	22.55	52	290	292	294
Penta (Cl_5) PCBs	26.25	101	324	326	328
Hexa (Cl_6) PCBs	29.95, 31.05	153, 138	358	360	362
Hepta (Cl_7) PCBs	33.95	180	394	396	398
Deca (Cl_{10}) PCBs (internal standard)	41.91	209	496	498	500

Table 2
IONS MONITORED IN GC-MS SIM MODE

from some extractible interfering elements, with a recovery of 50-120 %. The following performance parameters were studied: specificity, selectivity, repeatability, intermediary precision, recovery, detection limit and robustness [5-13].

The developed method is applicable in the concentration domain of 1-100 pg/mL PCB in water (1-100 ng/mL in the solution to be analyzed).

Experimental part

The development of GC-MS method for PCBs determination in water consisted in establishing of the separation conditions of the analyzed components from water matrix (at an adequate recovery), by liquid-liquid extraction, the establishing of the optimal GC-MS parameters and the validation of this method.

In the step of the analytes - matrix separation, PCBs from water samples prepared for analysis was extracted with hexane, carbon disulfide and chloroform through stirring at an appropriate speed followed by separating funnel separation. Anhydrous sodium sulfate was added over the resulting extract to remove water. The organic fractions were concentrated to a final volume of 10 mL at a constant vacuum, with a Kuderna-Denish evaporator for GC-MS analysis.

In the step II were established the optimal GC-MS separation parameters. The detection and quantitative determination by mass spectrometry, in the variant *Selected Ion Monitoring* (MS-SIR) was used.

Analysis method

The identification of the chromatographic peaks was carried out by comparing mass spectra obtained with the spectra in the library of the mass spectra of the system and on the basis of retention time. For the quantitative determination of PCBs was used internal standard method.

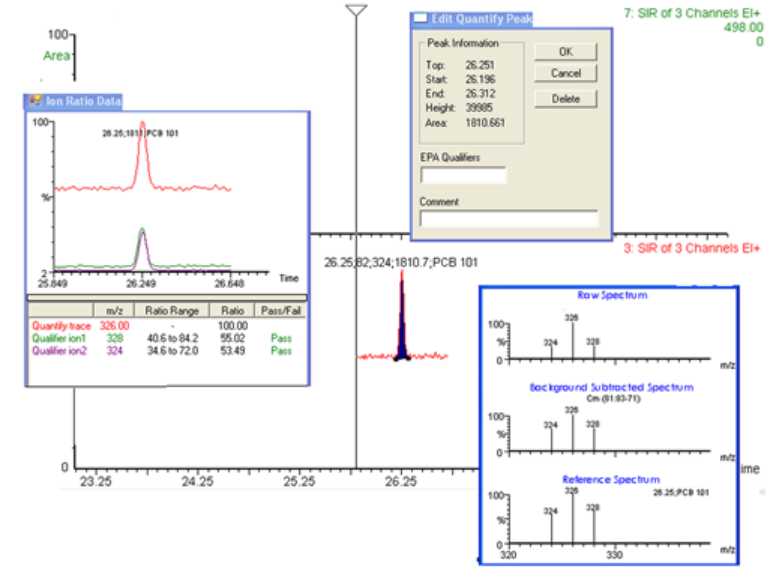

Fig. 2. PCB 101 quantify and qualifier ions, integration range and peak area

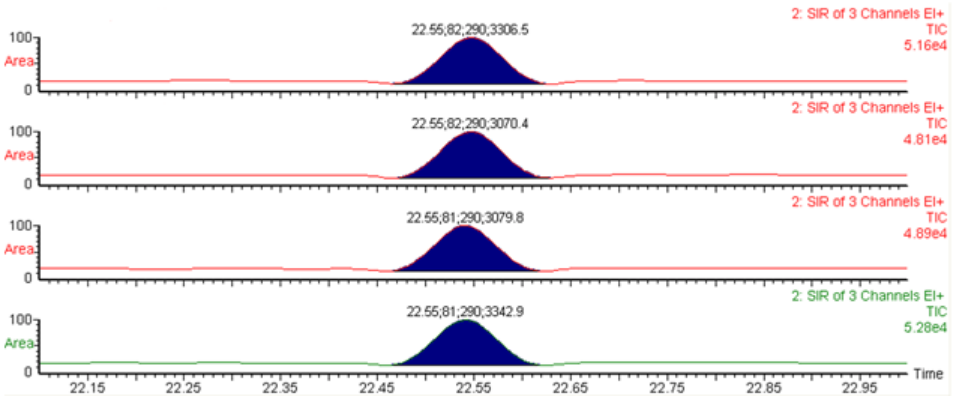

Fig. 3. Repeatability for PCB 52 standard of 5 ng/mL

PCB 52 concentration 5ng/ml	Area (µV·s)
Standard 1	3307
Standard 2	3070
Standard 3	3080
Standard 4	3343
Average	3200
Standard deviation	145
The coefficient of variation of the area (%)	4.5

Table 3
AREA COEFFICIENT OF VARIATION FOR PCB 52

Water samples were collected in amber glass flasks, with a capacity of 1.5 L. The *p*H was verified as it should be between 5 -7.5. Extraction was performed by shaking the sample flask followed by separation of the separating funnel. Its added 30 mL of solvent extraction over PCBs doped sample and its agitated for 15 min at a speed of 500 rev / min. Hexane was used as the extraction solvent in the first phase and then carbon disulfide and chloroform. The content was transferred into a 2 L separating funnel and it was allowed to stand for phase separation. The lower aqueous phase is passed back into the sample flask and the extraction is repeated twice with 30 mL of solvent. In the resulting extract was added anhydrous sodium sulfate and stirred for one minute. It was left to stand for five minutes after which the clarified extract was passed into the evaporator. The sodium sulfate was washed with 20 mL of additional solvent which was introduced in evaporator for concentration. Collected dried extract was evaporated up to 1 mL at a constant vacuum not greater than 340 mbar. After concentrating it was transferred the extract quantitatively into a 10 mL volumetric flask and it was completed the volume with solvent.

GC-MS analytical conditions

Chromatographic studies were obtained using a Perkin Elmer gas chromatograph coupled to a mass spectrometer. The mass spectrometer was operated in selected ion monitoring (SIM) mod with the m/z ratio(s) monitored for each analyte. Full GC-MS method and optimization parameters are given in table 1.

To identify each PCB retention time, 2 µL of a solution mixture of PCB 28, PCB 52, PCB 101, PCB 153, PCB 138 and PCB 180, concentration 10 µg/mL in isooctane, from Sigma Aldrich, was injected into the GC. The obtained results are presented in figure 1.

After identifying polychlorinated biphenyl by comparing the mass spectra obtained with spectra library of mass spectra of the system (NIST, NBS) are established the monitored ions in SIM, shown in table 2.

Results and discussions

The GC-MS-SIR instrument was calibrated in the specified conditions for the concentration domain of 1-100 ng/mL. To establish the regression curve and calculate the correlation coefficients were prepared 6 standards: 1 ng/mL, 5 ng/mL, 10 ng/mL, 20 ng/mL, 50 ng/mL, 100 ng/mL in hexane, which was add 1 mL internal standard. To prepare these standards was used a mixed solution of PCB 28, PCB 52, PCB 101, PCB 153, PCB 138, PCB 180, concentration 10 mg/mL in isooctane and a solution of

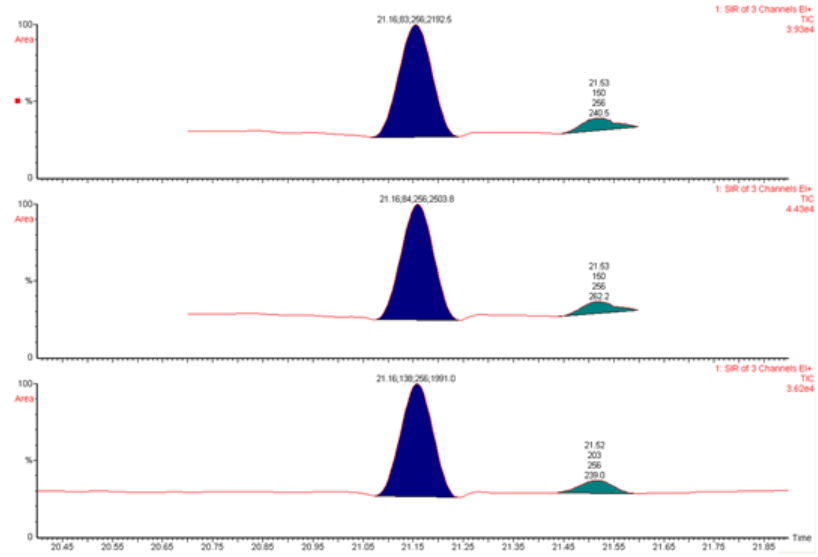

Fig. 4. PCB 28 standard of 1 ng/mL

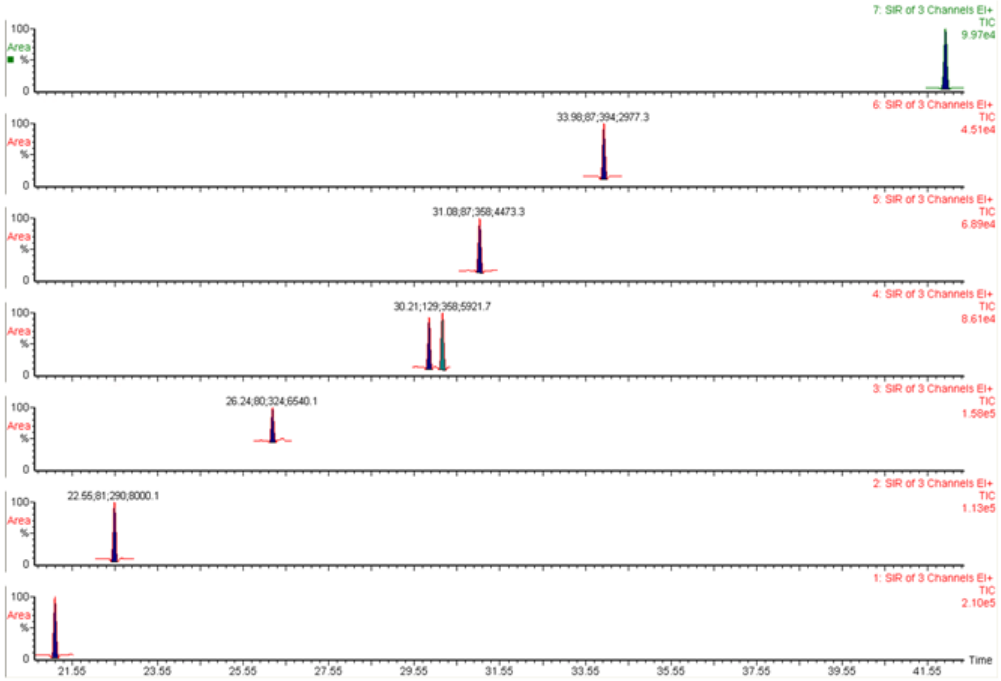

Fig. 5. SIM chromatograms for PCB 28, 52, 101, 138, 153, 180 standards 10 ng/mL in hexane

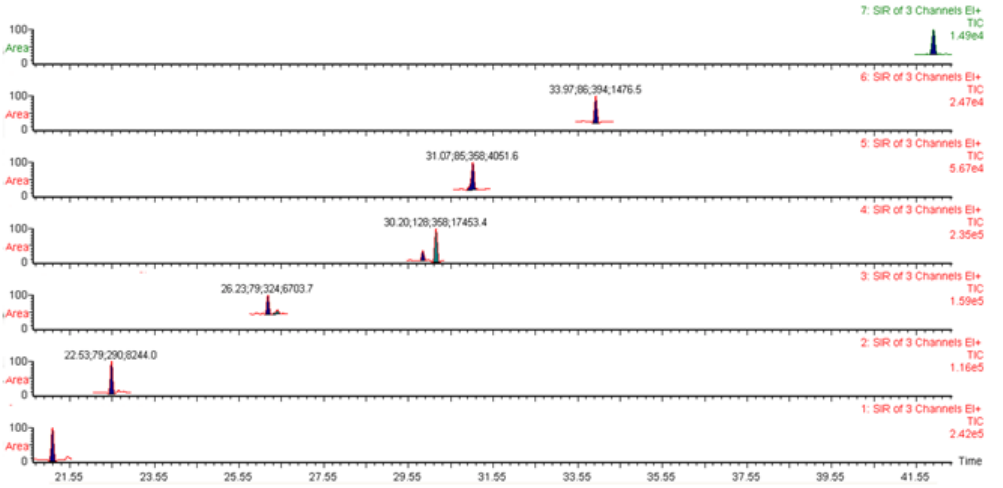

Fig. 6. The recovery: SIM chromatograms for PCB 28, 52, 101, 138, 153, 180 standards 10ng/mL from 1 L of water using hexane extraction solvent

PCB 209, nominal concentration 10 mg/mL in heptane purchased from Fluka.

The method linearity has been studied using the linearity by regression of the correlation $A_{ci}/A_{is} = f(concentration)$. For all calibration straight lines, the correlation coefficient is > 0.997, fact proving the linearity on the studied domain.

In figure 2 is presented the calibration curve data for PCB 101: qualifier and quantify ions, acceptable range, area and peak height and standard integration interval of 10 ng/mL.

To determine the repeatability, the chromatograms of 10 calibrating standards with the concentration of 5 ng/

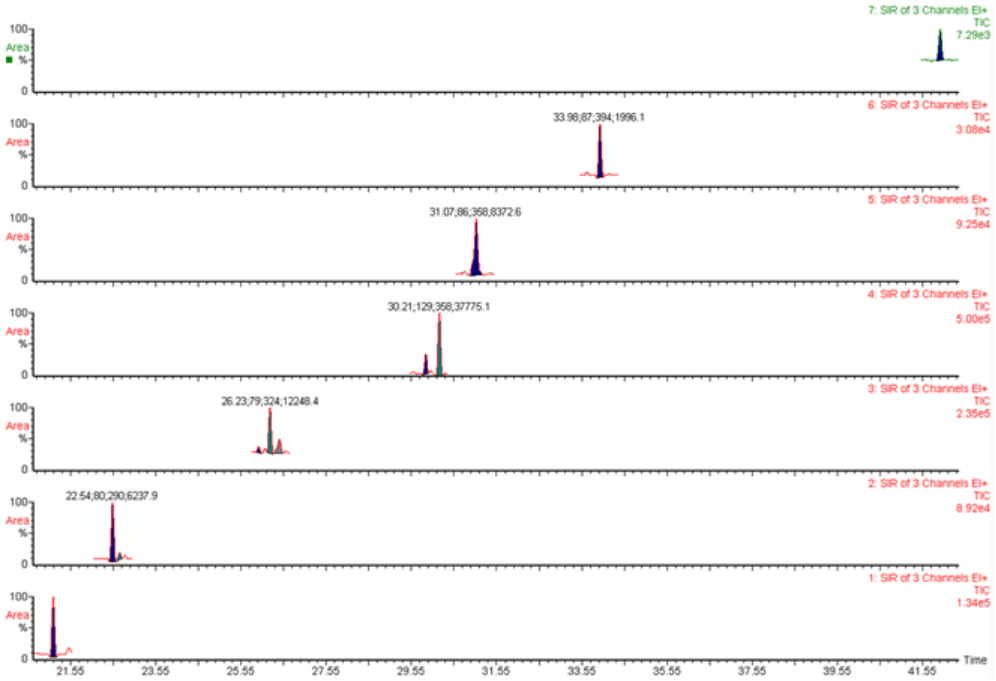

Fig.7. SIM chromatograms for PCB 28, 52, 101, 138, 153, 180 standards 10 ng/mL in carbon disulfide

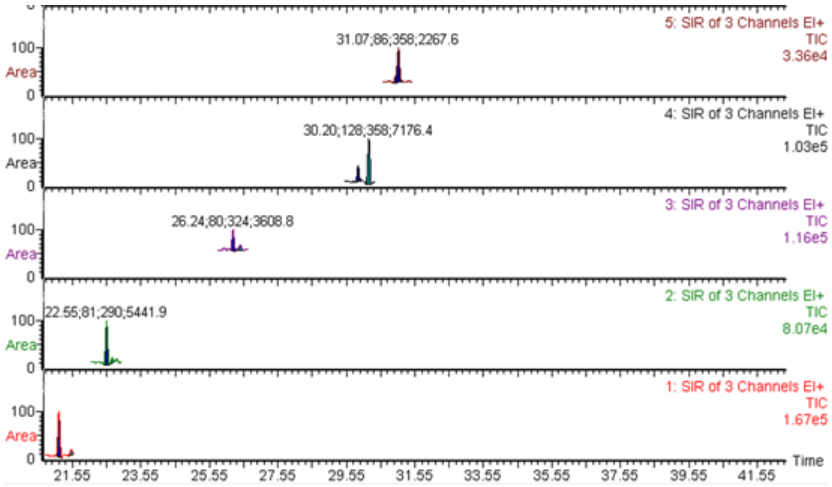

Fig. 8. The recovery: SIM chromarograms for PCB 28, 52, 101, 138, 180 standards 10 ng/mL from 1 L of water using carbon disulfide extraction solvent

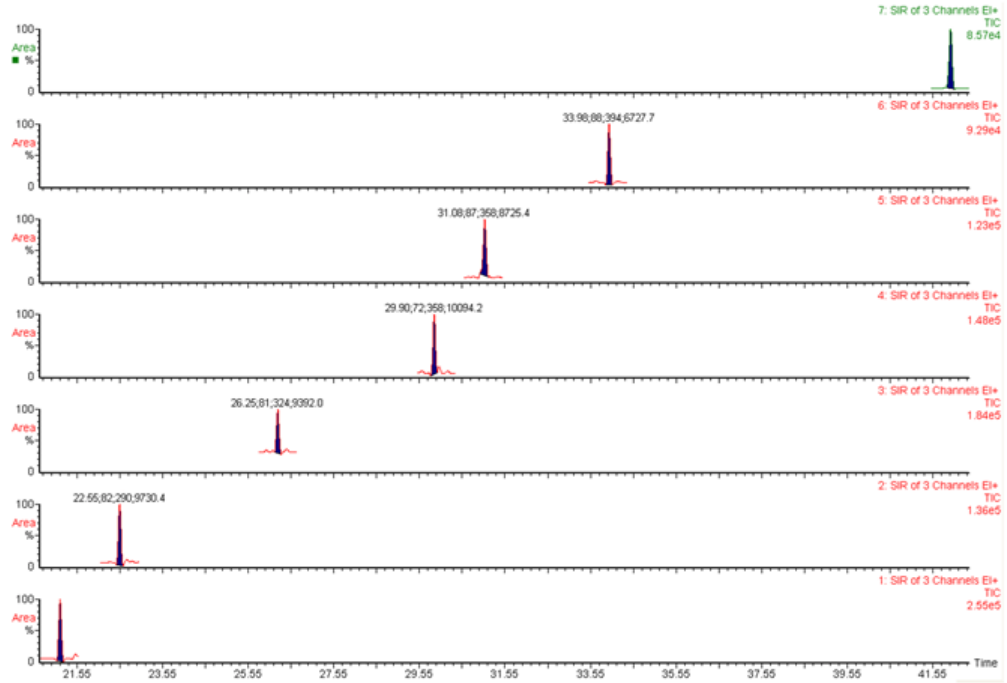

Fig. 9. SIM chromatograms for PCB 28, 52, 101, 138, 153, 180 standards 10 ng/mL in chloroform

mL, were recorded within a time interval as short as possible. Figure 3 indicates the repeatability obtained for PCB 52 standard of 5 ng/mL based on which was calculated the coefficient of variation of the area (table 3).

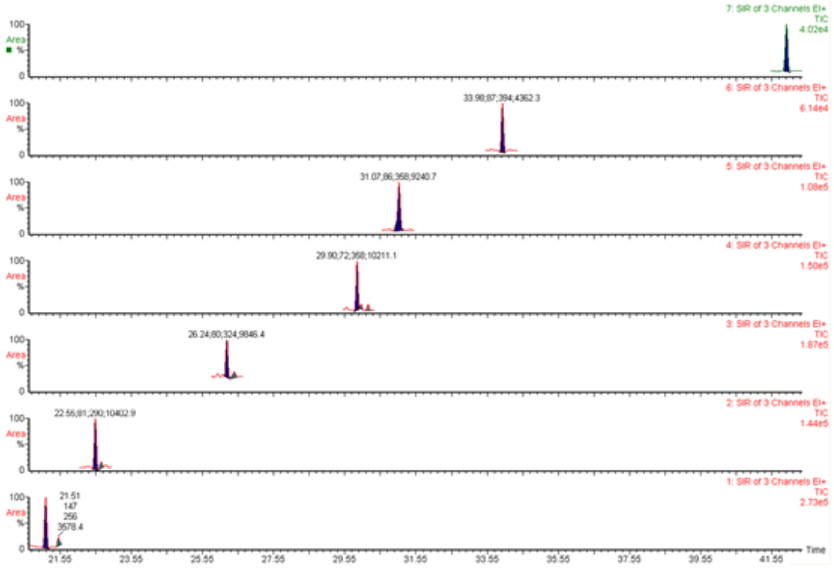

Fig. 10. The recovery: SIM chromatograms for PCB 28, 52, 101, 138, 153, 180 standards 10ng/mL from 1 L of water using chloroform extraction solvent

Table 4
PCB STANDARD OF 1 ng/mL

PCB	PCB standard area of 1 ng/ml (µv/s)					
	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6
PCB 28	1762	2166	1889	2985	2867	2934
PCB 52	749	894	786	1187	1165	1108
PCB 101	563	731	487	822	871	960
PCB 153	247	366	270	438	450	561
PCB 138	162	306	150	334	297	432
PCB 180	109	176	72	181	162	259

Table 5
THE RECOVERY OF THE PCB 28, 52, 101, 138, 153, 180 STANDARDS 10 ng/mL FROM 1 L OF WATER USING LIKE EXTRACTION SOLVENT HEXANE

Compound	Standard area 10ng/ml in hexane	Standard area 10 ng/ml in hexane from water sample	Recovery %
PCB 28	15297	17944	117.3
PCB 52	8000	8244	103.1
PCB 101	6540	6704	102.5
PCB 138	5921	5534	93.5
PCB 153	4473	4052	90.6
PCB 180	2977	1477	50.0

Table 6
THE RECOVERY OF THE PCB 28, 52, 101, 138, 153, 180 STANDARDS 10 ng/mL FROM 1 L OF WATER USING LIKE EXTRACTION CARBON DISULFIDE

Compound	Standard area 10ng/ml in carbon disulfide	Standard area 10 ng/ml in carbon disulfide from water sample	Recovery %
PCB 28	9495	12093	127.4
PCB 52	6238	5442	87.2
PCB 101	12248	3609	29.5
PCB 138	11737	2683	22.9
PCB 153	8373	2087	24.9
PCB 180	1996	734	36.9

To determine the detection limit, a calibrating standard of 1 ng/mL from PCB 52, PCB 101, PCB 153, PCB 138 and PCB 180 has been prepared and recorded, measuring the corresponding area. The values obtained are presented in figure 4.

In order to determine the PCBs recovery of the samples were used three series of standards of the PCBs 28, 52, 101, 138, 153, 180 of 10 ppb in the solution to be analyzed using extraction solvent like hexane, carbon disulfide and chloroform. Recovery levels obtained were between 50 and 117% for hexane (fig. 5-6), 37 and 127% for carbon

Table 7
THE RECOVERY OF THE PCB 28, 52, 101, 138, 153, 180 STANDARDS 10 ng/mL From 1 L OF WATER USING LIKE EXTRACTION SOLVENT CHLOROFORM

Compound	Standard area 10ng/ml in chloroform	Standard area 10 ng/ml in chloroform from water sample	Recovery %
PCB 28	18821	20890	111.0
PCB 52	9730	10403	106.9
PCB 101	9392	9846	104.8
PCB 138	10094	10211	101.1
PCB 153	8725	9241	105.9
PCB 180	6728	4362	64.8

disulfide (fig. 7-8) and 65 - 111% for chloroform (fig. 9-10). The obtained results are presented in table 5-7.

Conclusions

The development of GC-MS method for PCBs determination in water consisted in establishing of the separation conditions of the analyzed components from water matrix (at an adequate recovery), by liquid-liquid extraction, the establishing of the optimal GC-MS parameters and the validation of this method.

In the first step, the analytes-matrix separation, the PCBs from water samples prepared for analysis was extracted with hexane, carbon disulfide and chloroform.

In the step II were established the optimal GC-MS separation parameters. The detection and quantitative determination by mass spectrometry, in the variant Selected Ion Monitoring (MS-SIR) was used.

As the method has been developed in our laboratory, the method validation has been necessary by studying the following performance parameters: specificity, selectivity, repeatability, intermediary precision, recovery, detection limit and robustness.

The selectivity, determined as lack of interferences with the compounds of interest, was achieved through the repeatability of the gas chromatographic retention times and by quantification ion and qualifying ions from MS-SIR method. This improved selectivity eliminates interferences between PCBs and some chemical compounds in water matrix remaining after liquid-liquid extraction step and incomplete gas chromatographic separation.

It was determined the coefficient of variation of the area for standard 5 ng/mL for each PCB and this was comprised between 5-21%.

The method linearity has been studied, for all calibration straight lines, the correlation coefficient is > 0.997, fact proving the linearity on the studied domain.

The GC-MS-SIR method performs an adequate separation of PCBs from the water matrix and eliminates some extractible interfering elements with a recovery of 50-120 %. The method is applicable in the concentration range of 1-100 pg/mL PCB in water (1-100 ng/mL in the solution to be analyzed).

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