

Mass Spectrometric Study of the Bromination of Technical Mixtures of Polychlorinated Biphenyls

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Abstract—The products of bromination of polychlorinated biphenyls (PCBs) that constitute Trichlorobiphenyl and Sovol PCB technical mixtures were studied by gas chromatography–mass spectrometry. On the basis of mass spectrometric data, the reaction was shown to result in formation of a mixture of poly(bromo-chloro)biphenyls containing from one to five bromine atoms and from two to six chlorine atoms in different combinations. It was found that the content of monobromo derivatives increases while the content of di-, tri-, and tetrabromo PCB derivatives decreases when the chlorination degree of the initial PCBs increases.

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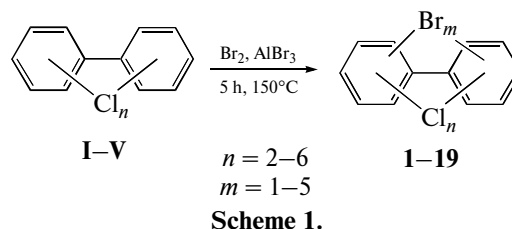
Polychlorinated biphenyls are known as persistent organic pollutants (POPs) and destined to processing or destruction [1]. But PCBs are valuable starting materials for preparing useful products. One of PCB processing methods is their chemical modification. The main PCB transformation processes are nucleophilic substitution reactions because they lead to substitution of chlorine atoms by functional groups (hydroxy, alkoxy, and carboxy), which potentially reduces the toxicity of resulting products [2]. The study of electrophilic substitution in PCBs has attracted much less attention because these reactions do not remove chlorine atoms from the substrates. Data on the nitration and sulfonation of technical PCB mixtures have been reported in [3, 4]. Nonetheless, the additional functional groups provide a possibility to involve PCB electrophilic substitution products into further reactions as intermediates [5]. One of such transformations is the carboxyethenylation of aromatic substrates by reacting acrylate esters with aryl halides under Heck reaction conditions [6] for constructing polymer matrices. Aryl bromides show the highest reactivity in these reactions.

The bromination of organic halide substrates under the action of bromine in the presence of Lewis acids is referred to as electrophilic substitution reactions. The aim of this work is to conduct mass spectrometric study of the products of bromination of Trichlorobi-

phenyl and Sovol technical PCB mixtures under electrophilic substitution conditions.

Trichlorobiphenyl PCB is a mixture of di-, tri-, tetra-, and pentachlorobiphenyls. It is an analog of foreign Arochlor 1242 PCB mixture [7] (Fig. 1). Sovol PCB is a mixture composed mainly of tetra-, penta-, and hexachlorobiphenyls [8] (Fig. 2).

It is known from literature that the bromination of PCBs under nucleophilic substitution conditions is not efficient [9]. In this work, we conducted a bromination of the PCB mixtures under electrophilic substitution condition to give mixtures of poly(bromo-chloro)biphenyls. The best results were obtained for the reactions of the PCB mixtures with bromine in the presence of aluminum bromide (Scheme 1). Table 1 shows the codes of initial PCBs in Trichlorobiphenyl and Sovol mixtures and their bromination products.



Scheme 1.

Figures 1 and 2 display the chromatograms of bromination products of the PCB mixtures. The bromo derivatives of PCBs were found to be eluted after initial PCBs. The retention time for the derivatives increases with the number of bromine atoms, which agrees well with data reported in the [9]. In some cases, several derivatives were eluted simultaneously.

The relative content of bromination products was assessed by the internal normalization of peak areas in chromatograms obtained by gas chromatography–

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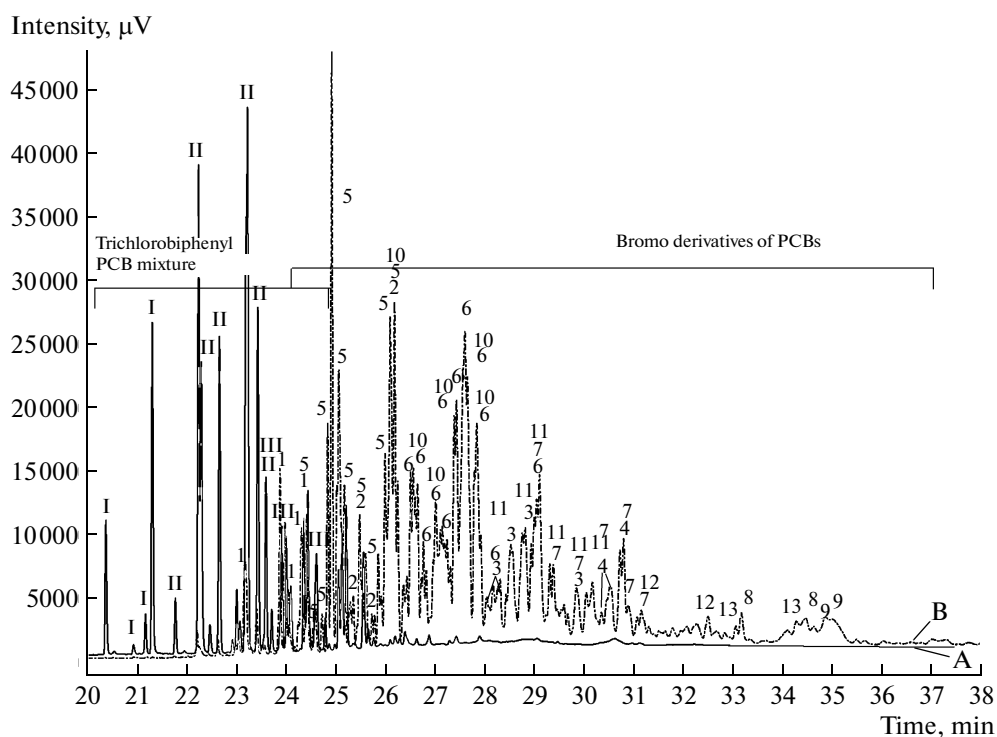


Fig. 1. Chromatograms of (A) Trichlorobiphenyl PCB mixture and (B) bromination products of Trichlorobiphenyl PCB mixture (codes of initial PCBs and PCB bromination products are given in Table 1).

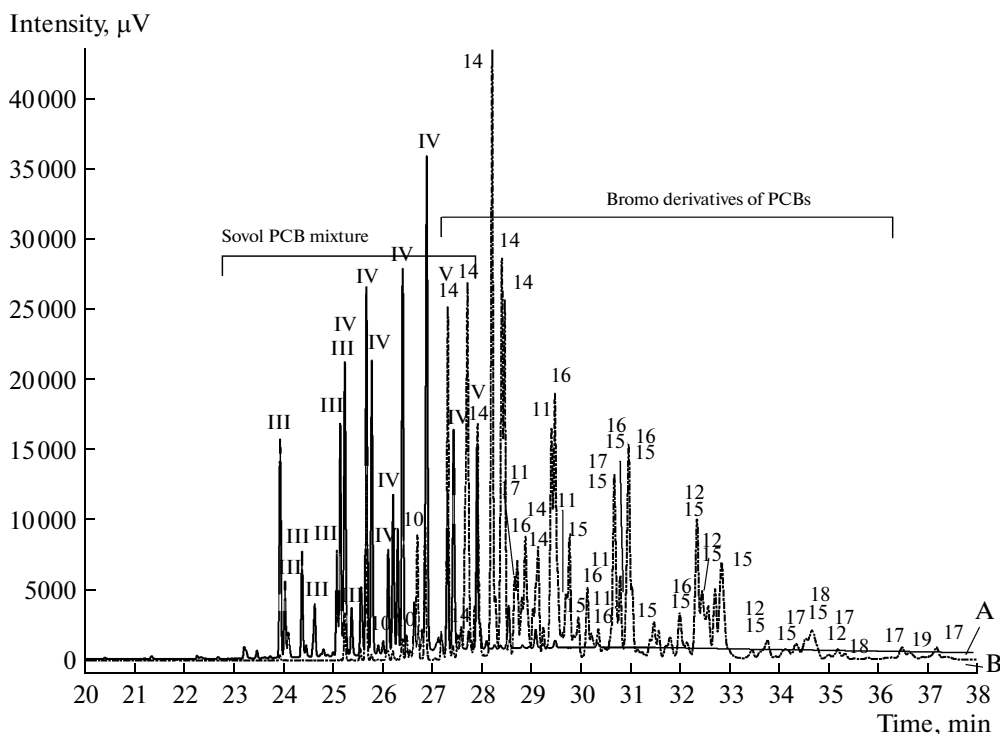


Fig. 2. Chromatograms of (A) Sovol PCB mixture and (B) bromination products of Sovol PCB mixture (codes of initial PCBs and PCB bromination products are given in Table 1).

mass spectrometry upon scanning over total ion current (Table 1).

The analysis of bromination products of Trichlorobiphenyl PCB mixture revealed that dichlorobiphe-

nyls (I) reacted completely, and the total peak area of unreacted tri- (II), tetra- (III), and pentachlorobiphenyls (IV) was less than 10% of total peak area of reaction products.

Table 1. Assessment of the relative content of the components in the bromination products of PCB mixtures

Code	Molecular formula	Molecular ion, <i>m/z</i>	Bromination products			
			Trichlorobiphenyl PCB mixture		Sovol PCB mixture	
			content, %	number of isomers	content, %	number of isomers
I	C ₁₂ H ₈ Cl ₂	222	—	—	—	—
1	C ₁₂ H ₇ Cl ₂ Br	300	2.7	6	—	—
2	C ₁₂ H ₆ Cl ₂ Br ₂	378	3.2	4	—	—
3	C ₁₂ H ₅ Cl ₂ Br ₃	456	6.5	4	—	—
4	C ₁₂ H ₄ Cl ₂ Br ₄	534	0.8	2	—	—
II	C ₁₂ H ₇ Cl ₃	256	2.1	5	—	—
5	C ₁₂ H ₆ Cl ₃ Br	334	24.1	12	—	—
6	C ₁₂ H ₅ Cl ₃ Br ₂	412	25.9	12	—	—
7	C ₁₂ H ₄ Cl ₃ Br ₃	490	3.5	7	—	—
8	C ₁₂ H ₃ Cl ₃ Br ₄	568	0.3	2	—	—
9	C ₁₂ H ₂ Cl ₃ Br ₅	646	0.2	2	—	—
III	C ₁₂ H ₆ Cl ₄	290	5.8	2	—	—
10	C ₁₂ H ₅ Cl ₄ Br	368	13.0	5	1.9	3
11	C ₁₂ H ₄ Cl ₄ Br ₂	446	9.2	6	8.4	7
12	C ₁₂ H ₃ Cl ₄ Br ₃	524	0.5	2	3.2	5
13	C ₁₂ H ₂ Cl ₄ Br ₄	602	0.3	2	—	—
IV	C ₁₂ H ₅ Cl ₅	324	0.5	1	3.0	4
14	C ₁₂ H ₄ Cl ₅ Br	402	0.1	2	35.0	12
15	C ₁₂ H ₃ Cl ₅ Br ₂	480	—	—	18.9	17
16	C ₁₂ H ₂ Cl ₅ Br ₃	558	—	—	1.3	4
V	C ₁₂ H ₄ Cl ₆	358	—	—	8.5	5
17	C ₁₂ H ₃ Cl ₆ Br	436	—	—	15.0	12
18	C ₁₂ H ₂ Cl ₆ Br ₂	514	—	—	1.3	4
19	C ₁₂ HCl ₆ Br ₃	592	—	—	0.2	1

A total of 69 peaks of PCB bromo derivatives resulted from Trichlorobiphenyl mixture were identified. Dichlorobiphenyls were shown to produce mono- (**1**), di- (**2**), tri- (**3**), and tetrabromo derivatives (**4**); tribromodichlorobiphenyls formed in the largest amount. Trichlorobiphenyls form mono- (**5**), di- (**6**), tri- (**7**), tetra- (**8**), and pentabromo derivatives (**9**); the content of mono- and dibromo derivatives is virtually the same and their total peak area is tenfold of the total peak area of tri-, tetra-, and pentabromo derivatives. Tetrachlorobiphenyls produce mono- (**10**), di- (**11**), tri- (**12**), and tetrabromo derivatives (**13**), monobromo derivatives being the main products. Only two peaks of monobromo derivative (**14**) were identified among pentachlorobiphenyls reaction products.

The analysis of bromination products for Sovol PCB mixture revealed that tetrachlorobiphenyls (**III**) reacted completely, while the total peak area of unre-

acted penta- (**IV**) and hexachlorobiphenyls (**V**) was less than 12% of total peak area of reaction products.

A total of 65 peaks of bromo derivatives were identified in Sovol PCB bromination mixture. Tetrachlorobiphenyls were shown to produce mono- (**10**), di- (**11**), and tribromo (**12**) derivatives, dibromotetrachlorobiphenyls are the major components. Pentachlorobiphenyls also produce mono- (**14**), di- (**15**), and tribromo derivatives (**16**), but the total area of peaks of monobromo derivatives is twice as high as that for dibromo derivatives. Hexachlorobiphenyls produce mono- (**17**) and dibromo derivatives (**18**), and the total peak area of the dibromo derivatives is almost 10 times smaller than that of the monobromo derivatives. One peak of the hexachlorobiphenyl derivative containing three bromine atoms (**19**) was detected, its area was less than 0.1% of the total area of product peaks.

Table 2. Peak distribution in multiplets of molecular ions of poly(bromochloro)biphenyls

Derivative	Molecular ion multiplets, $m/z/I^{rel}$, %								
	M	M + 2	M + 4	M + 6	M + 8	M + 10	M + 12	M + 14	M + 16
C ₁₂ H ₇ Cl ₂ Br	300/52	302/100	304/48	306/5					
C ₁₂ H ₆ Cl ₂ Br ₂	378/38	380/100	382/91	384/29	386/4				
C ₁₂ H ₅ Cl ₂ Br ₃	456/19	458/74	460/100	462/66	464/20	466/1			
C ₁₂ H ₄ Cl ₂ Br ₄	534/15	536/7	538/100	540/90	542/41	544/12	546/1		
C ₁₂ H ₆ Cl ₃ Br	334/53	336/100	338/63	340/17	342/2				
C ₁₂ H ₅ Cl ₃ Br ₂	412/33	414/95	416/100	418/51	420/12	422/1			
C ₁₂ H ₄ Cl ₃ Br ₃	490/18	492/65	494/100	496/79	498/31	500/6	502/1		
C ₁₂ H ₃ Cl ₃ Br ₄	568/10	570/51	572/100	574/96	576/57	578/17	580/3		
C ₁₂ H ₂ Cl ₃ Br ₅	646/18	648/64	650/100	652/56	654/32	656/13	658/2		
C ₁₂ H ₅ Cl ₄ Br	368/44	370/100	372/83	374/30	376/5	378/1			
C ₁₂ H ₄ Cl ₄ Br ₂	446/24	448/78	450/100	452/61	454/19	456/4			
C ₁₂ H ₃ Cl ₄ Br ₃	524/12	526/69	528/100	530/81	532/52	534/11	536/3	538/1	
C ₁₂ H ₂ Cl ₄ Br ₄	602/9	604/32	606/72	608/100	610/49	612/33	614/8	616/2	
C ₁₂ H ₄ Cl ₅ Br	402/38	404/98	406/100	408/49	410/14	412/2			
C ₁₂ H ₃ Cl ₅ Br ₂	480/21	482/71	484/100	486/82	488/32	490/9	492/1		
C ₁₂ H ₂ Cl ₅ Br ₃	558/13	560/60	562/100	564/95	566/58	568/25	570/5	572/1	
C ₁₂ H ₃ Cl ₆ Br	436/29	438/80	440/100	442/59	444/23	446/5	448/2	450/1	
C ₁₂ H ₂ Cl ₆ Br ₂	514/17	516/63	518/100	520/90	522/46	524/17	526/5	528/1	
C ₁₂ HCl ₆ Br ₃	592/13	594/37	596/75	598/100	600/60	602/41	604/10	606/4	608/1

The mass spectra of brominated PCBs exhibit strong peaks of molecular ions. Due to particular chlorine and bromine isotope abundance, whose ratio is 3 : 1 for ³⁵Cl and ³⁷Cl and 1 : 1 for ⁷⁹Br and ⁸¹Br, the composition of molecular ion multiplets is very complex and peak distribution is shown in Table 2. The majority of identified PCB bromo derivatives were shown to display [M + 4]⁺ peak of maximal intensity. It was also found that the number of peaks in molecular ion multiplet increases with the number of chlorine and bromine atoms in molecule and reaches [M + 16]⁺. The highest peak in molecular ion multiplet is the basic peak in the entire mass spectrum of PCB bromo derivative.

The fragmentation of molecular ions of brominated PCBs (under electron impact) was found to take place via elimination of chlorine and/or bromine atoms in different combinations irrespective of their number in derivative molecule. Halogen atoms are eliminated first, benzene rings decompose next. Fragmentation features observed in the obtained mass spectra correspond to those reported in [9] for the mass spectra of monobromononachlorobiphenyl. Figure 3 displays the mass spectra of dibromotri- and tetrachlorobiphenyls, while Table 3 exhibits mass

spectral data for the brominated derivatives of trichlorobiphenyls.

Thus, in this work we confirmed the formation of poly(bromochloro)biphenyls upon bromination of PCBs on the basis of mass spectrometric data. It was found that the content of di-, tri-, and tetrabromo derivatives decreases, while the content of monobromo derivatives of PCBs increases, when the chlorination extent of initial PCBs rises. Poly(bromochloro)biphenyls obtained under these conditions from PCBs can be further subjected to carboxyethenylation and can be used as intermediate products for preparing valuable materials, polyphenylstyrenes [10].

EXPERIMENTAL

Identification and quantitative assessment of PCB bromination products. A Trace GC Ultra DSQ II gas chromatograph–mass spectrometer (USA) with a Thermo TR-5ms capillary column 30 m long, 0.25 mm in diameter, 0.25 μm thick film, and quadrupole mass-spectrometry detector was used. Total ion current scanning was performed in the mass range 20–1000 Da in electron impact mode (70 eV). Column temperature: initial, 40°C (keeping for 3 min), then programmed at a rate of 10 K/min up to 280°C (keeping for 30 min);

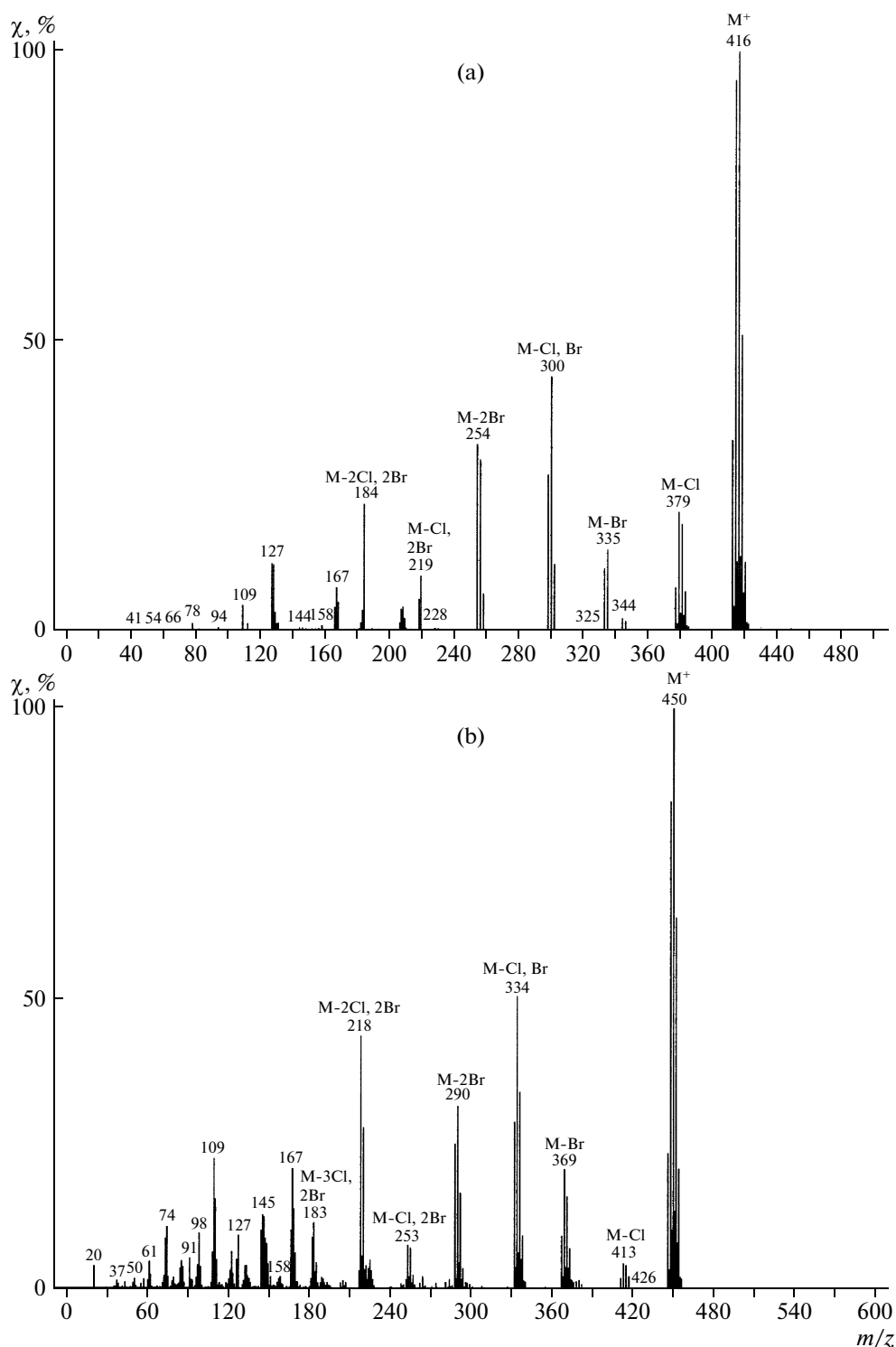


Fig. 3. Mass spectra of dibromo derivative of (a) trichlorobiphenyl $C_{12}H_5Cl_3Br_2$ and (b) tetrachlorobiphenyl $C_{12}H_4Cl_4Br_2$.

injector temperature, 250°C; detector temperature, 200°C; transition line temperature, 200°C. Helium was used as a carrier gas; split ratio, 1 : 50; flow rate through the column, 1.0 cm^3/min .

Bromination reaction procedure. Aluminum bromide (0.3 mmol) and 6 mmol of bromine was added to

3 mmol of PCB mixture (Trichlorobiphenyl mixture was considered to have formula $C_{12}H_7Cl_3$, Sovol mixture was considered as $C_{12}H_5Cl_3$), the mixture was gradually heated to 150°C for 5 h. Two grams of ice and 2 mL of concentrated hydrochloric acid was added to the reaction mixture, the reaction products

Table 3. Data of mass spectra of brominated trichlorobiphenyls

Ion	<i>m/z/I, %*</i>				
	C ₁₂ H ₆ Cl ₃ Br	C ₁₂ H ₅ Cl ₃ Br ₂	C ₁₂ H ₄ Cl ₃ Br ₃	C ₁₂ H ₃ Cl ₃ Br ₄	C ₁₂ H ₂ Cl ₃ Br ₅
M	334/100	412/100	490/100	568/100	646/100
M–Cl	299/14	377/21	455/8	533/12	611/11
M–Br	255/14	333/14	411/5	489/55	567/47
M–Br–Cl	220/83	298/44	376/27	454/32	532/18
M–Br–2Cl	185/14	–	–	–	–
M–Br–3Cl	150/38	–	–	–	–
M–2Br	–	254/32	332/11	410/40	488/34
M–2Br–Cl	–	219/10	297/2	375/5	453/4
M–2Br–2Cl	–	184/22	262/5	340/7	418/9
M–2Br–3Cl	–	149/20	227/10	305/6	383/7
M–3Br	–	–	218/32	–	–
M–3Br–Cl	–	–	183/12	296/30	374/32
M–3Br–2Cl	–	–	148/10	261/5	339/6
M–3Br–3Cl	–	–	113/7	226/13	304/1
M–4Br	–	–	–	252/21	330/28
M–4Br–Cl	–	–	–	217/10	295/7
M–4Br–2Cl	–	–	–	182/12	260/21
M–4Br–3Cl	–	–	–	147/14	225/6
M–5Br–Cl	–	–	–	–	216/19
M–5Br–3Cl	–	–	–	–	146/16

* Relative intensity (*I*, %) is shown for the ion with the maximal intensity in the cluster.

were extracted with carbon tetrachloride 2 × 10 mL. The extract was washed with 20% sodium hydroxide solution until complete discoloration and dried with sodium sulfate.

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