American Journal of Applied Chemistry
2019; 7(3): 104-109
http://www.sciencepublishinggroup.com/j/ajac
doi: 10.11648/j.ajac.20190703.14
ISSN: 2330-8753 (Print); ISSN: 2330-8745 (Online)

Methodology Article

Determination of Short Chain Chlorinated Paraffins in Textile Samples by GC-MS

Zeng Zheng, Shao Yuwan, Li Xian, Du Juan*

College of Chemistry, Chemical Engineering and Biotechnolohy, Donghua University, Shanghai, China

Email address:

zz@dhu.edu.cn (Zeng Zheng), shaoyw@dhu.edu.cn (Shao Yuwan), lixian@dhu.edu.cn (Li Xian), dujuan@dhu.edu.cn (Du Juan)

*Corresponding author

To cite this article:

Zeng Zheng, Shao Yuwan, Li Xian, Du Juan. Determination of Short Chain Chlorinated Paraffins in Textile Samples by GC-MS. *American Journal of Applied Chemistry.* Vol. 7, No. 3, 2019, pp. 104-109. doi: 10.11648/j.ajac.20190703.14

Received: May 7, 2019; **Accepted**: June 13, 2019; **Published**: July 8, 2019

Abstract: The method of determining short-chain chlorinated paraffins in textiles by GC-MS was established. Short-chain chlorinated paraffins, short for SCCPs, are a mixture of polychlorinated n-alkanes. These high production volume chemicals are widely used as leather coating, plasticizers for PVC and chlorinated rubber and flame retardants for plastics and textile. Due to their toxicity, as well as capacity for bioaccumulation and persistence in the environmental residue, SCCPs have become an obviously environmental issue. The current analytical equipment combination are very expensive and require a lot of laboratory space and advanced skills for operation, a ready-to-use commercially available method with relatively short time and satisfactory sensitivity urge to be established. In this new method, samples were extracted by n-hexane under ultrasonic followed by concentration and constant-volume and then identified by GC-MS and quantified by external standard method. With this method, a good linear relationship was found between 5 μg/mL ~30μg/mL with a linear correlation coefficient (R^2) above 0.995. The detection limit for SCCPs by this method was found to be as low as 10mg/kg. The recoveries of SCCPs in textiles at three levels which covers low, media and high concentration ranges are ranged from 82.3% to 106.9% with relative standard deviation (RSD) of 3.41%~7.61%(RSD, N = 6).

Keywords: Short-chain Chlorinated Paraffins, SCCPs, Determination, Quantification, GC-MS

1. Introduction

The chemical compounds defined as chlorinated paraffins (CPs), also knowns as polychlorinated alkanes (PCA), are a complex mixture of different chlorinated hydrocarbons with variable composition, first introduced to the market in the 1930s. [1] This group contains many congeners with different carbon chain length from C10 to C30, diverse chlorination degree from 40% to 70% by weight, as well as structural and spatial isomers. [2] The classification of CPs in general is based on chain length and is divided into three general groups: (1) short-chain CPs (SCCPs), which chain length range from C10 to C13; (2) medium-chain CPs (MCCPs)), which chain length range from C14 to C17; (3) long-chain CPs (LCCPs), which chain length are above C17. [3]

Industrial synthesis of SCCPs are conducted by ways of chlorination of petroleum-based n-alkanes/paraffins, olefin and alkyne fractions. [4] Because of their chemical and thermal stabilities, SCCPs are often used as flame retardants, plasticizers, and additives in paints, sealants and metal working fluids. [4] SCCPs have been listed as candidate persistent organic pollutants (POPs) in the Stockholm Convention due to their persistence, bioaccumulation and toxicity. [5] The use of SCCPs in metal- and leather product has been restricted in the European Union since 2004 because of high toxicities. [6] In recent years, several international and national law regulations on the manufacturing process and application of SCCPs have been introduced. [7] Oeko-Tex Standard 100 has imposed restrictions in SCCPs within 0.1% since 2011and highlighted their mass concentration to 100mg/kg in 2008. [8] DeTox organization also require its concentration in ecological textile within the limitation of 50mg/kg. [9]

Recently, the most reliable approach are single column gas

chromatography coupled with appropriate detectors including gas chromatography and mass spectrometer (GC-MS) [/10], gas chromatography-electron capture negative chemical ion source low/high resolution mass spectrometry (GC-ECNI-LRMS/HRMS) and gas chromatography-electron impact ionization mass spectrometry (GC-EI-MS) 11] and final determination with gas chromatography-flame ionization detector (GC-FID). [12] According to the Determination of Short-chain Chlorinated Paraffins in Textiles for Import and Export, ultrasonic extraction with n-hexane prior to the identification with gas chromatography-negative chemical ionization-mass spectrometry (GC-NICI-MS) and the quantification with gas chromatography-flame ionization detector (GC-FID). [13] This determination only processes in basis of the application of time-consuming and finance-consuming extraction techniques and purification solution. Having regard to the above-mentioned methods, it should be noticed that the optimal determination of the content level of SCCPs in samples requires a lot of financial resources. There is still a lack of a clearly defined, optimized and validated analytical methods which might be implemented in everyday analytical laboratory practice in studies of SCCPs' occurrence. [14]

2. Experimental Methods

2.1. Instruments and Solvents

Instruments: 7890A-5975C Gas Chromatography (Agilent Technologies Corporation, USA); BSA224S-CW Analytical Balance (Sartorius Lab Instruments GmbH & Co. KG, Germany); Rotary Evaporator (Heidolph Corporation, USA); SK82101HC Ultrasonic Cleaner (Shanghai Kudos Ultrasonic instrument co., ltd, China).

Solvents: SCCPs (51.5%Cl), SCCPs (55.5%Cl), SCCPs (63%Cl) standard solutions (100mg/L Dr. Ehren-storfer Corporation, Germany), n-hexane, acetone (All above solvents are chromatographically pure).

2.2. Preparation for Standard Solution

0.5, 1.0, 1.5, 2.0, 3.0mL standard solutions were transferred to volumetric flask respectively and then diluted by n-hexane to 10mL mark. The mass concentrations of these solutions were 5, 10, 15, 20, 30 μg/mL respectively.

2.3. Preparation for Textile Samples

Sample preparation is performed by reference to the Determination of Short-chain Chlorinated Paraffins in Textiles for Import and Export. Representative cloth samples were cut into 5mm*5mm pieces and weighed out 1g samples. 50mL n-hexane was added in and extracted by Ultrasonic Cleaner for 30min in the room temperature. The extraction liquid was filtered through the sand core funnel into a flat bottom flask. Wash the sample again by 30mL n-hexane. After combination and concentration with a rotary evaporator, 2mL n-hexane was added in precisely. Sufficient shaking and homogenization was pre-requisite and then the sample was collected into a vial with the 0.22um filter membrane.

2.4. Experimental Methods

Samples were analyzed on a 7890A-5975C Gas Chromatography (Agilent Technologies Corporation, USA). Chromatographic separation was achieved on a DM-5MS capillary column (30m*0.32mm*0.25um). The carrier gas was helium (99.9999% purity) and the column flow was maintained at 1mL min^{-1} using an electronic flow controller. The oven temperature was programmed at 100°C (3min) to 270°C with the heating rate of 20°C/min. The temperature of the GC-MS interface was held at 290°C, and the mass spectrometer was operated in EI mode at 70ev. The mass spectra were obtained from 50 to 550 amu.

The chromatograms of SCCPs (51.5%Cl), SCCPs (55.5%Cl), SCCPs (63%Cl) standard solutions were presented in figure 1.

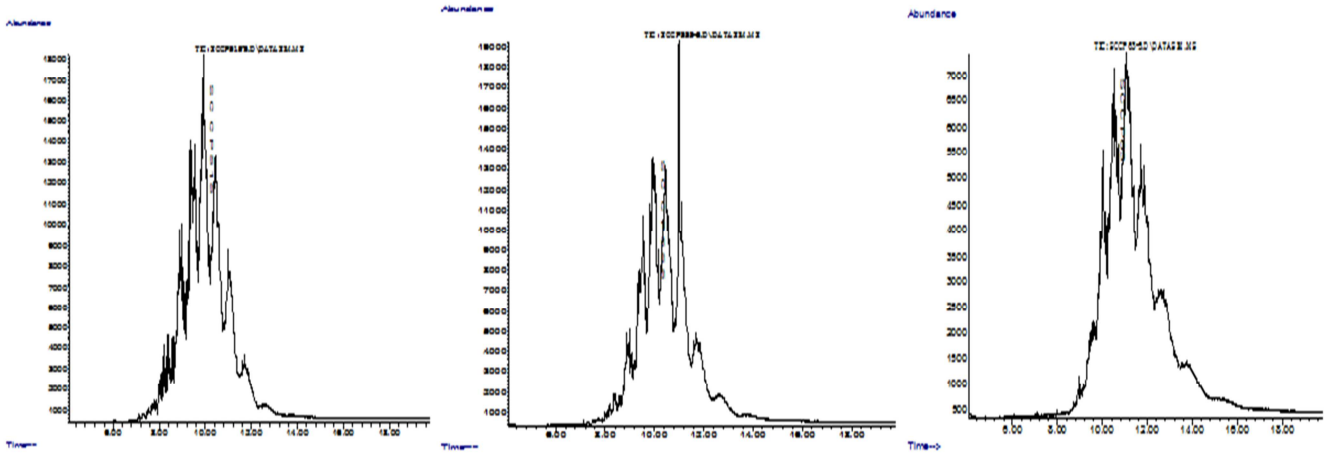

Figure 1. *The chromatograms of SCCPs (51.5%Cl), SCCPs (55.5%Cl), SCCPs (63%Cl).*

2.5. Identification and Quantification of SCCPs in Textile Samples

The positive SCCPs was confirmed by comparing the peak shape and mass spectrometry of the sample with that of the standard samples. The curve of standard SCCPs solution whose retention time was close to that of sample's was selected for quantitative analysis. And the concentration was calculated by the ion peak area with m/z of 89. The mass fraction of SCCPs from sample is calculated by the formula (1) below.

$$X = \frac{c \times V}{m} \quad (1)$$

while:

X is content of SCCPs in the samples, mg/kg;

c—concentration of SCCPs in samples, mg/L;

V—volume of samples, mL;

m—mass samples, g;

3. Result and Discussion

3.1. Optimization of Experimental Conditions-The Choose of Chromatographic Columns

With carbon chains length from C10 to C13, SCCPs are weakly polar substance, which are performed suitable by chromatographic column with weak polarity.

This study verified the detection and separation of SCCPs by chromatographic column DB-35MS and DB-5MS. DB-5MS displayed better separation and higher instrumental responsiveness. Their chromatograms were presented in figure 2 and figure 3.

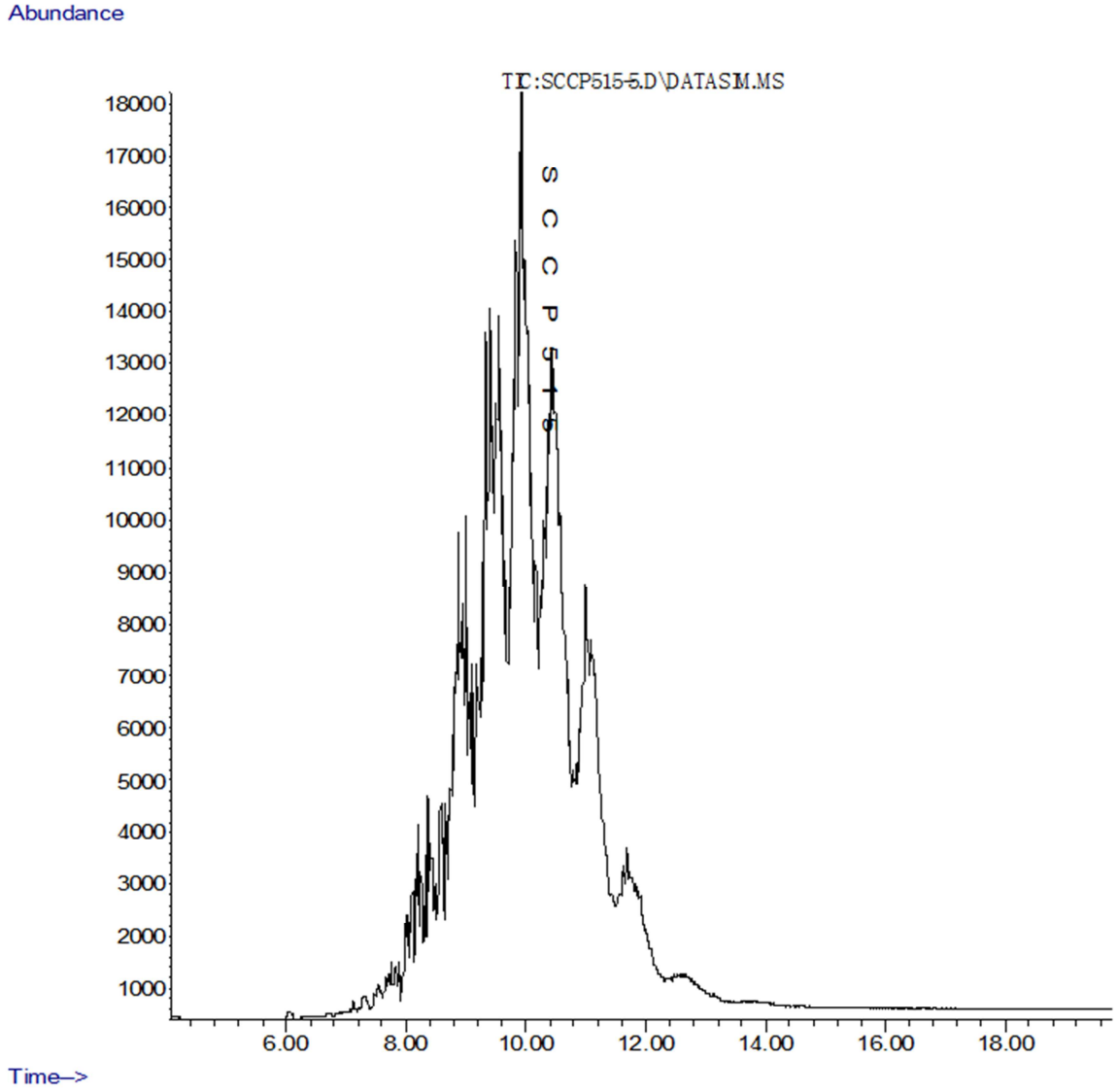

Figure 2. *Chromatographic of SCCPs (51.5%) with DB-35MS column.*

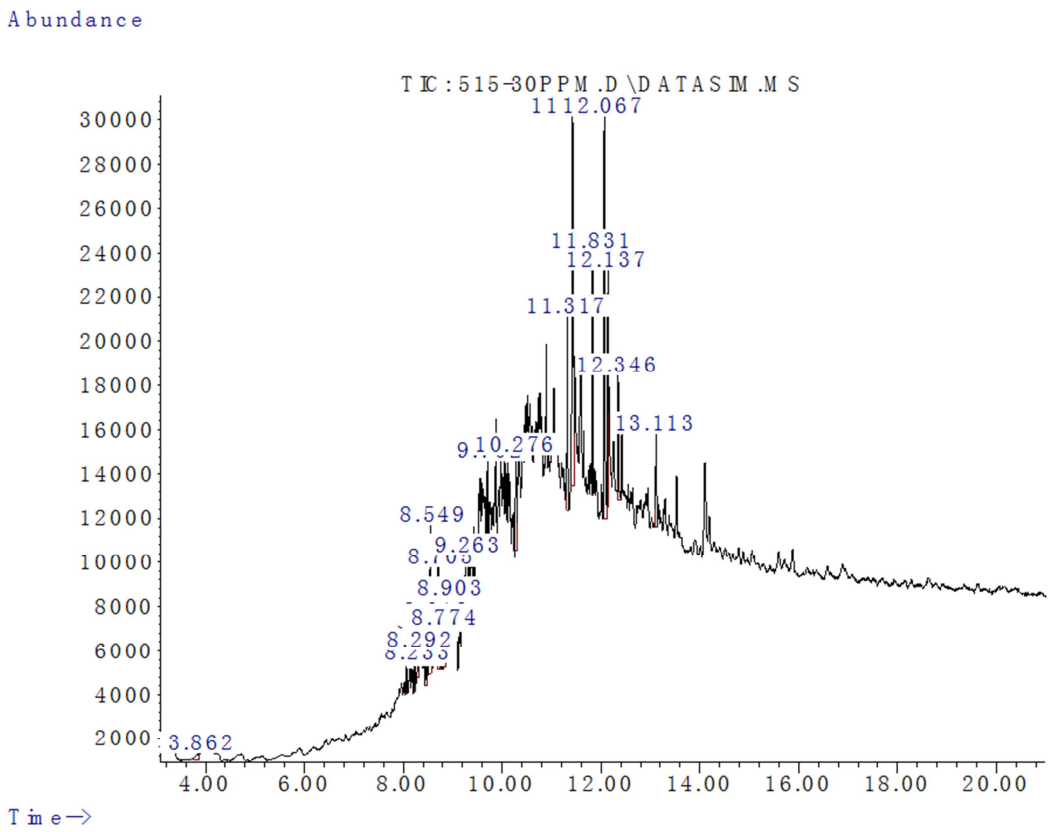

Figure 3. *Chromatographic of SCCPs (51.5%) with DB-5MS column.*

3.2. Linear Relationship

The series of SCCPs (51.5%Cl), SCCPs (55.5%Cl), SCCPs (63%Cl) standard solutions with mass concentrations of 5, 10, 15, 20, 30 μg/mL were determined. The standard curves were drawn. The following table display the linear equations and linear correlation coefficients.

With this method, a good linear relationship was found over a wide mass concentration range from 5 to 30 μg/mL, with a linear correlation coefficient (R^2) of 0.998.

Table 1. *Linear equation of standard curve and R^2 about SCCPs.*

Standard Solution	Linear Equation	Correlation Coefficient
SCCPs (51.5%)	y=23200x-13800	0.998
SCCPs (55.5%)	y=34000x+96700	0.998
SCCPs (63%)	y=31600x-1160	0.998

3.3. Detection Limits

The samples were quantified by the external standard method in which the blank samples were added with 10 times lowest detective concentration. Standard deviation (SD) was calculated based on the actual SCCPs contents in the samples. The Method Detection Limit (MDL) was expressed as 10 times SD. Results are displayed in the Table 2.

Table 2. *The method detection limit (MDL).*

No.	Results of External Standard Method		
	SCCPs (51.5%)/ mg/kg	SCCPs (55.5%)/mg/kg	SCCPs (63%)/ mg/kg
1	10.81	10.58	9.15
2	8.84	9.26	8.70
3	9.91	10.04	10.62
4	10.22	9.86	9.76
5	9.40	8.98	10.04
6	9.95	10.31	9.70
7	8.96	9.17	9.00
8	9.33	10.87	9.76
9	8.53	9.42	9.30
10	10.46	8.79	10.84
MDL (10SD)	9.64	9.73	9.69

The experimental results indicated that the detection limits of SCCPs (51.5%Cl), SCCPs (55.5%Cl), SCCPs (63%Cl) standard samples by this method were 9.64mg/kg, 9.73 mg/kg and 9.69 mg/kg respectively. Considering the linear relationship and samples' quality the method detection limit was 10 mg/kg. The limited concentration of SCCPs required by Oeko-Tex Standard 100 and DeTox organization are 100mg/kg and 50mg/kg respectively. [15] Therefore, this method detection limits met the requirements for the detection of SCCPs in ecological textiles.

3.4. Recovery and Precision

SCCPs standard solutions with certain known concentrations were added into the samples for recovery experiments. These recovery experiments covered high, medium and low levels with the labeled mass concentrations were 10, 30 and 60mg/kg respectively. For each sample, the experiments were conducted at least six times to confirm the reproducibility of the reported procedures. The value of SCCPs were calculated in the following Table3.

Table 3. *Results of Recovery Experiments.*

Concentrations of Standard Solutions		SCCPs (51.5%)		SCCPs (55.5%)		SCCPs (63%)	
		Results/mg/kg	Recovery Rates/%	Results/mg/kg	Recovery Rates/%	Results/mg/kg	Recovery Rates/%
10mg/kg	1	10.81	108.1	10.58	105.8	9.15	91.5
	6	8.84	88.4	9.26	92.6	8.70	87.0
	3	9.91	99.1	10.04	100.4	10.62	106.2
	4	10.22	102.2	9.86	98.6	9.76	97.6
	5	9.40	94.0	8.98	89.8	10.04	100.4
	6	9.95	99.5	10.31	103.1	9.70	97.0
Precision /%		7.76		7.31		7.06	
30mg/kg	1	28.24	94.1	29.29	97.6	27.82	92.7
	6	26.01	86.7	26.18	87.3	26.18	87.3
	3	32.08	106.9	28.58	95.3	28.24	94.1
	4	27.82	92.7	29.42	98.1	28.90	96.3
	5	26.49	88.3	30.10	100.3	27.56	91.9
	6	28.49	95.0	27.59	92.0	28.48	94.9
Precision /%		7.61		5.02		3.41	
60mg/kg	1	54.26	90.4	57.10	95.2	59.05	98.4
	6	56.09	93.5	54.50	90.8	51.82	86.4
	3	59.59	99.3	51.14	85.2	54.16	90.3
	4	49.38	82.3	53.46	89.1	54.88	91.5
	5	52.22	87.0	58.76	97.9	57.81	96.3
	6	55.94	93.2	55.42	92.4	60.56	100.9
Precision /%		6.45		4.89		5.86	

The detection limit for SCCPs by this method was found to be as low as 10mg/kg, and the average recoveries for SCCPs varied from 83.2% to 106.9% with precision of 3.41% to 7.76%.

4. Conclusion

According to the literature data, the appropriate SCCP analysis, especially the reliable quantification process, is an important issue and an analytical challenge. [16] The authors developed a valuable method with which to appropriately quantify SCCPs in textile samples.

This method undertakes identification and quantification of short-chain chlorinated paraffins in textiles by GC-MS with the detection limit of 10mg/kg. This method represented a good linear relationship over a mass concentration range from 5 to 30 μg/mL with a linear correlation coefficient (R^2) of 0.998.

In this new method, 5mm*5mm representative cloth samples were weighed out 1g. And then samples were extracted by n-hexane under ultrasonic followed by concentration and constant-volume and then identified by GC-MS and quantified by external standard method. In Optimization experiments weak polar chromatographic column (DB-5MS) represented better separation and higher instrumental responsiveness.

The samples were quantified by the external standard method in which the blank samples were added with 10 times lowest detective concentration. The SCCPs in samples were confirmed by comparing the peak shape and mass spectrometry with that of the standard samples. The retention time of samples were selected for quantitative analysis. And the concentration was calculated by the ion peak area with m/z of 89.

Recovery experiments covered high, medium and low levels with the labeled mass concentrations were 10, 30 and 60mg/kg respectively. The recoveries of SCCPs in textiles at three levels which covers low, media and high concentration ranges are ranged from 82.3% to 106.9% with relative standard deviation (RSD) of 3.41%~7.61%(RSD, N = 6). he method presented low detection limit, good accuracy and precision, and was suitable for determination of SCCPs in textiles.

References

[1] Yuan, B.; Muir, D.; MacLeod, M., Methods for trace analysis of short-, medium-, and long-chain chlorinated paraffins: Critical review and recommendations. Anal Chim Acta 2019, 1074, 16-32.

[2] Li, H.; Fu, J.; Pan, W.; Wang, P.; Li, Y.; Zhang, Q.; Wang, Y.; Zhang, A.; Liang, Y.; Jiang, G., Environmental behaviour of short-chain chlorinated paraffins in aquatic and terrestrial ecosystems of Ny-Alesund and London Island, Svalbard, in the Arctic. Sci Total Environ 2017, 590-591, 163-170.

[3] Casa, M. V.; van Mourik, L. M.; Weijs, L.; Mueller, J.; Nash, S. B., First detection of short-chain chlorinated paraffins (SCCPs) in humpback whales (Megaptera novaeangliae) foraging in Antarctic waters. Environ Pollut 2019, 250, 953-959.

[4] Xin, S.; Gao, W.; Cao, D.; Lv, K.; Liu, Y.; Zhao, C.; Wang, Y.; Jiang, G., The thermal transformation mechanism of chlorinated paraffins: An experimental and density functional theory study. J Environ Sci (China) 2019, 75, 378-387.

[5] Wang, X. T.; Jia, H. H.; Hu, B. P.; Cheng, H. X.; Zhou, Y.; Fu, R., Occurrence, sources, partitioning and ecological risk of short- and medium-chain chlorinated paraffins in river water and sediments in Shanghai. Sci Total Environ 2019, 653, 475-484.

[6] van Mourik, L. M.; Gaus, C.; Leonards, P. E. G.; de Boer, J., Chlorinated paraffins in the environment: A review on their production, fate, levels and trends between 2010 and 2015. Chemosphere 2016, 155, 415-428.

[7] Sun, R.; Luo, X.; Tang, B.; Li, Z.; Huang, L.; Wang, T.; Mai, B., Short-chain chlorinated paraffins in marine organisms from the Pearl River Estuary in South China: Residue levels and interspecies differences. Sci Total Environ 2016, 553, 196-203.

[8] Li, H.; Li, J.; Li, H.; Yu, H.; Yang, L.; Chen, X.; Cai, Z., Seasonal variations and inhalation risk assessment of short-chain chlorinated paraffins in PM2.5 of Jinan, China. Environ Pollut 2019, 245, 325-330.

[9] i, Q.; Cheng, X.; Cui, Y.; Sun, J.; Li, J.; Zhang, G., Short- and medium-chain chlorinated paraffins in the Henan section of the Yellow River: Occurrences, fates, and fluxes. Sci Total Environ 2018, 640-641, 1312-1319.

[10] Kalinowska, K.; Lenartowicz, P.; Namiesnik, J.; Marc, M., Analytical procedures for short chain chlorinated paraffins determination - How to make them greener? Sci Total Environ 2019, 671, 309-323.

[11] Gherghel, S.; Morgan, R. M.; Arrebola-Liebanas, J.; Romero-Gonzalez, R.; Blackman, C. S.; Garrido-Frenich, A.; Parkin, I. P., Development of a HS-SPME/GC-MS method for the analysis of volatile organic compounds from fabrics for forensic reconstruction applications. Forensic Sci Int 2018, 290, 207-218.

[12] Ma, W.; Rajput, G.; Pan, M.; Lin, F.; Zhong, L.; Chen, G., Pyrolysis of typical MSW components by Py-GC/MS and TG-FTIR. Fuel 2019, 251, 693-708.

[13] Parera, J.; Abalos, M.; Santos, F. J.; Galceran, M. T.; Abad, E., Polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls, paraffins and polybrominated diphenyl ethers in marine fish species from Ebro River Delta (Spain). Chemosphere 2013, 93 (3), 499-505.

[14] Gao, Y.; Zhang, H.; Chen, J.; Zhang, Q.; Tian, Y.; Qi, P.; Yu, Z., Optimized cleanup method for the determination of short chain polychlorinated n-alkanes in sediments by high resolution gas chromatography/electron capture negative ion-low resolution mass spectrometry. Anal Chim Acta 2011, 703 (2), 187-93.

[15] Luo, X. J.; Sun, Y. X.; Wu, J. P.; Chen, S. J.; Mai, B. X., Short-chain chlorinated paraffins in terrestrial bird species inhabiting an e-waste recycling site in South China. Environ Pollut 2015, 198, 41-6.

[16] Ma, X.; Chen, C.; Zhang, H.; Gao, Y.; Wang, Z.; Yao, Z.; Chen, J.; Chen, J., Congener-specific distribution and bioaccumulation of short-chain chlorinated paraffins in sediments and bivalves of the Bohai Sea, China. Mar Pollut Bull 2014, 79 (1-2), 299-304.