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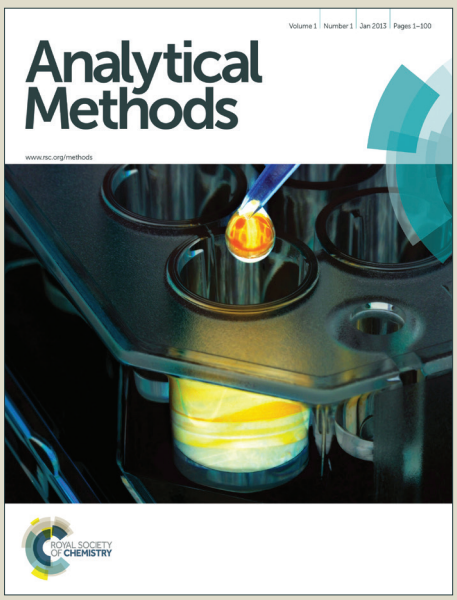

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Determination of butyltin and phenyltin compounds in sea products by Grignard derivatization and gas chromatography-triple quadrupole tandem mass spectrometry

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Abstract

A robust method for the determination of six organotin compounds (OTs), monobutyltin (MBT), dibutyltin (DBT), tributyltin (TBT), monophenyltin (MPhT), diphenyltin (DPhT) and triphenyltin (TPhT), in sea products was developed using gas chromatography-triple quadrupole tandem mass (GC-MS/MS). The target compounds were extracted by hexane containing 0.01% tropolone, derivatizated by Grignard reagent n-PrMgBr, purified on a serial connection of silica and florisil SPE columns and finally analyzed by GC-MS/MS. Enhanced sensitivity and selectivity were acquired using MS/MS than the single MS method, especially for the reducing of complex interferences in biotic matrices. The limits of detection (LODs) for six OTs were all lower than 0.1 μgSn kg^{-1} for wet samples and the LODs were not higher than 0.5 μgSn kg^{-1} for dry samples. The linearity loefficients (r^2) for the six OTs were all above 0.999 within the linear range from 0.4 to 200 μgSn kg^{-1}. The accuracy of the method was extensively validated by the determination of a certified reference material-CE477 and a spiked recovery test in four different biotic matrices, including tonguefishes, patinopecten yessoensis, neverita didyma and Asia moon scallop. The determined butyltin concentrations of CE477 agreed well with the certified values and the relative standard deviations (RSDs) for the six OTs were all below 12.1%. The spiked recoveries in four biotic matrices were in the range of 70.5-105.3% for MBT, DBT, TBT, DPhT and TPhT, and 82.2-133.5% for MPhT, and the RSDs ranged from 0.5% to 12.5%. The proposed methodology was applied to the determination of butyltin and phenyltin compounds in nine different sea products sampled from Bohai coast, China, with the total OTs ranging from 1.36 to 20.54 μgSn kg^{-1} wet weight.

Key words: organotin, speciation, sea product, Grignard derivatization, gas chromatography-triple quadrupole tandem mass.

Introduction

Organotin compounds are one of the most toxic classes of contaminants released into the marine environment by human activities [1]. Tributyltin (TBT) and triphenyltin (TPhT) are the main species and they have been widely used as biocides in antifouling paints for boats [2, 3]. The toxic potential of OTs to non-target organisms, including adverse effects on reproduction, development, nervous systems, immune systems and endocrine systems, are well documented [4]. It is worth notice that TBT and TPhT are both implicated as endocrine disruptors and they can cause imposex of marine gastropods[5, 6]. Although the OTs were worldwide banned as boicides in antifouling systems by International Maritime Organization (IMO) [7], the long time persistence and their potential to bioaccumulation are still of concern [8]. Food, especially seafood, is considered the primary source of OTs to human [9-11].

For the speciation of OTs in complex matrix, such as sediments or biota, sample pretreatment procedures are always needed, including extraction, derivatization and purification. A variety of extraction methods were reviewed, and extraction with organic solvents (hexane, dichloromethane or methanol) containing acid (HCl or HAc) and complexing agents（tropolone was most commonly used）was the most extensively used method for both biotic and abiotic matrices [1]. Purification is necessary for removal of lipids, pigments, proteins, sulfur and high boiling point compounds, and the most commonly used adsorbents are silica, florisil and alumina [3]. Derivatization is very important for organotin speciation by GC method. Three groups of derivatization methods are always used, including alkylation with Grignard reagents, ethylation by sodium tetraethylborate ($NaBEt_4$), and hydride generation with $NaBH_4$ or KBH_4. Among the three

derivatization methods, hyride generation and ethylation with $NaBEt_4$ have advantage of being directly applicable to aqueous samples and simutaneous derivatization/extraction is possible, while their yields of derivatization are always very low for solid samples. In contrast to that, Grignard derivatization was proven to have high derivatization yields for organotin speciation in a large variety of matrices (water, sediments and biota) [12].

Hyphenated technology has been developed as the main tool for identification and quantification of OTs. The most commonly used technique is capillary gas chromatography (GC) because of the following reasons: Firstly, the separation ability of this method is stronger than liquid chromatography (LC). Derivatization is not needed for LC, while its application is not as wide as GC due to its lower sensitivity and its poor power to separate chemicals [13]. Then, the GC method can be easily coupled with several element-specific detectors, such as atomic absorption spectrometry (AAS) [14], flame photometric detection (FPD) [15, 16], pulse flame photometric detection (PFPD) [16, 17], atomic emission spectrometry (AES) [18], mass spectrometry (MS) [19, 20], or inductively-coupled plasma mass spectrometry (ICP-MS) [21, 22]. Among the methods described above, ICP-MS was considered as the most sensitive technique, FPD and MS were both extensively used for their high sensitivity and selectivity. As the development of mass spectrometry in recent years, MS/MS was also used in organotin speciation in several studies, and even lower detection limits and higher selectivity were reported [23-27]. While as far as we know, the MS/MS methods were limited to ion trap tandem mass and the triple quadrupole tandem mass technique was seldom used in organotin speciation，especially for biotic samples.

The present study described a method using Grignard derivatization combined with gas chromatography-triple quadrupole tandem mass spectrometry for the speciation of butyltin and

phenyltin compounds in sea products. The specific advantages of using MS/MS for the analysis of OTs were demonstrated compared to the traditional MS method. The analytical performance of the proposed method was evaluated and the method was successfully applied to real samples.

1. Experimental

2.1 Reagent and materials

All the standards, monobutyltin trichloride (MBT, 97%), dibutyltin dichloride (DBT, 96%), tributyltin chloride (TBT, 97%), tetrabutyltin (TeBT, 96.5%, as internal standard), monophenyltin trichloride (MPhT, 98.5%), diphenyltin dichloride (DPhT, 97%) and triphenyltin chloride (TPhT, 96%) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The stock standard solutions were prepared as 1 gSn L^{-1} in methanol and stored at -20 ^{0}C in the dark. Working solutions of 1 mgSn L^{-1} were prepared by a gradual dilution of the stock solutions with ultra pure water. The Grignard reagent of n-propylmagnesium bromide (n-PrMgBr, ca. 2.0 M, in tetrahydrofuran) and Tropolone (99%) were purchased from Tokyo Chemical Industry (TCI), Japan. All reagents and solvents used were of analytical grade or better. All glassware was cleaned overnight in 50% (v/v) nitric acid solution and rinsed with ultra pure water.

The Solid phase extraction (SPE) columns used for sample cleanup were obtained from Dikma Technologies Inc., USA. Two types of columns were used, including ProElut Silica (1 g, 6 ml) and ProElut Florisil (1 g, 6 ml). The combination of the two columns gave a very good purification performance for all the selected samples.

2.2 Instrumentation

Organotin compounds were determined using an Agilent 7890 gas chromatograph coupled with Waters Quattro micro triple quadrupole mass spectrometry. The gas chromatography conditions were as follows: butyltin and phenyltin compounds were separated on a capillary column (DB-1701, 30 m×0.25 mm×0.25 μm); the injector temperature was set at 290 ^{0}C in splitless mode; high purity helium (≥99.999%) was used as the carrier gas at a constant flow rate of 1.5 mL/min; the oven temperature was initially set at 40 ^{0}C for 1 min, then programmed at 30 ^{0}C/min to 280 ^{0}C and held for 3 min; the transfer line temperature was set as 280 ^{0}C.

Mass spectrometry was operated in Electron Impact (EI) mode, and the ionization energy was 70 eV. The signal acquisition mode was Multiple Reaction Monitoring (MRM) with which two parent-daughter ion transitions were monitored for qualitative and quantitative determination (Table 1). The scanned mass ranged from 50 to 450 u at 0.5s/scan for the full scan mode. For the selected ion monitoring (SIM) mode of GC-MS, three ions were monitored for each compound (Table 1).

Table 1

A SA300 shaker (Yamato, Japan) was used for the extraction of organotin compounds from sea products. The compounds under study were derivatizated with the assistance of an 8893 ultrasonic cleaner (Cole-Parmer, USA). The sample cleanup was conducted on an SPE Vacuum Manifold (Phenomenex, USA). The other apparatuses used for sample preparation were as follows: R-215 rotary vacuum evaporator (Büchi, Switzerland), KDC-40 low speed centrifuge (USTC chuangxin Co. Ltd., Zonkia Branch), N-EVAP112 nitrogen evaporator (Organomation Associates, Jnc, USA),

and Milli-Q highly pure water generation system (Millipore Co., USA).

2.3 Sample preparation procedure

The sample preparation procedure was based on a former reported method [28] with a few modifications. Briefly, 5.0 g homogenized wet sample (or 1.0 g dry sample) was placed in a 50 mL glass centrifugal tube, then 500 μL internal standards (IS) were introduced and mixed with the sample. Then 10 mL THF-HCl (20:1) solution was added to digest the sample. After a 5 min vigorous shaking, 20 mL of 0.01% tropolone-hexane (m/v) was introduced and a 40 min shaking was conducted. Then after a 3 min centrifugation on a speed of 3000 *rmp*, the upper layer organic phase was gently transferred to a heart-shaped bottle. Then 10 mL hexane was added and extracted for another 10 min. The combined extract was concentrated to about 2 mL by a rotary evaporator. Then 1 mL of n-PrMgBr was mixed with the extract and sonicated for 15 min at room temperature, and then 5 mL 0.5 M sulfur acid was added dropwise under col d water bath to decompose the exess n-PrMgBr. The solution was transferred to a 10 mL tube and centrifugated at 3500 rmp for 5 min. The supernatant liquid was transferred to an activated silica SPE column, and eluted with 10 mL hexane. After concentration to about 1 mL, a further purification was conducted on a Florisil column by the same procedure. The eluant was gently concentrated to 1 mL under a nitrogen stream. Finally, 1 μL of the solution was directly injected into the GC for analysis.

The calibration was performed using TeBT as internal standard. Calibration plots from 0.2 to 200 μgSn kg^{-1} for each analyte, and the whole sample preparation procedure was conducted for each calibration point.

2. Results and Discussion

3.1 Sample pretreatment

The main improvements compared to the former method [28] are as follows. Firstly, a centrifugation was introduced after the shaking, which is good for phase separation and for further improving extration efficiency. Then, a commercial Grignard reagent n-PrMgBr was used in this method, which has proven to have a good devivatizating yield. Finally, a solid-phase extraction on the basis of two commercial SPE columns was used in this work instead of the fommer self-packed cartridge. The elution of propylated organotin compounds on silica and florisil column was investigated and the result is shown in Fig. 1. To ensure all object compounds were eluted, an elution voloume of 10 mL was finally chosen for both columns.

Figure 1

3.2 Gas chromatography-triple quadrupole tandem mass spectrometry

The propylated organotin compounds were separated on a DB-1701 capillary column. After optimization of the GC conditions, all seven compounds were baseline separated and the total chromatographic analytical time was no more than 12 minutes (Fig. 2C), which ensure a fast method in routine analysis.

The triple quadrupole tandem mass spectrometer was operated in multiple reaction monitoring (MRM) mode and the detailed conditions are revealed in Table 1. The optimization of the MRM is as follows. Firstly, the parent ions for each analyte were selected through the mass spectra of full scanning (see supporting information SI-1). The specific ions with high *m/z* and high abudance

were always chosen. Then, a daughters scanning was conducted with different collision energies, from which (see supporting information SI-2) the optimized daughter ions and the corresponding collision energies were obtained. Finally, two parent-daughter ion pairs were selected for each compound and they were both applied for the qualitative and quantitative analysis.

The application of triple quadrupole tandem mass spectrometry obviously enhanced the selectivity of the method for organotin speciation. To vertify this, a traditional GC-MS qualitative method was introduced and compared.

After sample pretreatment, there are still lots of interferences exist in the sample solutions, including coextractants from the matrix, impurity substances in Grignard reagent and the unexpected derivatizating products [12]. The complex interferences were clarified in Fig. 2A. Numerous peaks of intererences can be seen in the chromatograph, and most of the organotin peaks were drown. The chromatogram obtained in the selected ion recording mode by single MS is shown in Fig. 2B. There are still lots of unknown peaks and the background noises are still high, indicating a poor analytical performance by GC-MS. When the tandem mass spectrometry was used, a very clean chromatograph was acquired, which is shown in Fig. 2C. The background noise in this figure is quite low and the interfences are almost totally eliminated. The high sensitivity of tandem mass is mainly due to the progressive enhancement of selectivity for the object compounds in the multiple reactions monitoring (MRM) mode.

Figure 2

3.3 Analytical performance

The analytical performance of organotin determination by Grignard derivatization and GC-MS/MS is shown in Table 2. The method was applied to both dry and wet samples. As shown in Table 2, for wet sample, the limits of detection were as low as 0.1 μgSn kg^{-1} for most compounds except for DPhT, which is even lower to 0.05 μgSn kg^{-1}. As to dry samples, the LODs were 0.5 μgSn kg^{-1} for MBT, DBT, TBT, MPhT and TPhT，and 0.25μgSn kg^{-1} for DPhT. The sensitivities of the method for butyltin and phenyltin compounds are comparable or better than the former reported methods (Table 3).

Table 2

Table 3

The main advantage of the method, using Grignard derivatization and GC-MS/MS, is the ability of eliminating complex interferences, which ensure a good accuracy for the biotic sample analysis. The validation of the method was conducted by the analysis of organotin compounds in a certified reference material-CE477. Three butyltin compounds were certified, and the results obtained by the proposed method are in accord well with the certified values (Table 2). The concentration of three phenyltin species are also displayed, which were also reported in several studies. The levels detected by Lv etal [31] were 0.623±0.023, not detected, and 0.635±0.023 mgSnkg^{-1} for MPhT, DPhT and TPhT, respectively. And the results obtained by Zhao etal [35] were 0.482±0.029, not detected, and 0.484±0.028 mgSnkg^{-1} for each phenyltin. Compared to the data showed in table 2, all these results are different from each other but in the same order, indicating that phenyltins

could be detected in CE-477 but the concentrations are not stable. Maybe this is the reason why the phenyltins were not certified in CE-477. The relative standard deviations (RSDs) of six OTs are all below 12.1%, indicating a good repeatbility of the method.

The application of the proposed method was further evaluated by a spiked recovery test in different kinds of sea products, including two wet samples and two dry samples. Two spiked levels were investigated for each sample. The average recoveries are shown in Table 4. The spiked recoveries were in the range of 70.5-105.3% for MBT, DBT, TBT, DPhT and TPhT, and 82.2-133.5% for MPhT, and the RSDs ranged from 0.5% to 12.5%, indicating a good accuracy and the proposed method could be applied to both wet and dry samples.

Table 4

3.4 Application to real samples

The Grignard derivatization and GC-MS/MS method was applied for the determination of butyltin and phenyltin compounds in nine sea products obtained from a dock in Qinhuangdao, a city along the Bohai Bay of China. The results are displayed in Table 5. OTs was detected in all the 9 wet samples, with the concentration ranging from 1.36 to 20.54 μgSn kg^{-1}. The level is comparable to the former studies [10, 11], which may indicate low risk for consumers. However, the potential health risk should still draw attention. As to the species, TBT and TPhT were detected in all samples and were dominant species. It is evident that the proposed method is universally available for the determination of organotin compounds in sea products.

Table 5

3. Conclusions

A method using Grignard derivatization and gas chromatography coupled with triple quadrupole tandem mass spectrometry was developed for the speciation of butyltin and phenyltin compounds in sea products. The substantially enhancement of selectivity is the predominant advantage of MS/MS compared to the traditional single MS. The LODs for all six organotin compounds were 0.05-0.1 μgSn kg^{-1} (wet weight). The spiked recoveries in four different biotic matrices were in the range of 70.5-105.3% (except for MPhT, which were ranged from 82.2% to 133.5%) and the RSDs were all below 12.5%. Also, the determined butyltin values by the proposed method agreed well with the certified values of the certified reference material-CE477. All these results indicate that the sensitivity, repeatbility and selectivity of the method are all satisfactory. The proposed method could be applied for organotin speciation in various sea products, and it would be benefit for further studies on organotin pollution in seafoods.

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Table 1 The GC-MS/MS and GC-MS conditions for the speciation of butyltins and phenyltins.

Compounds	Quantification Trace (CE [a], eV)	Secondary Trace (CE, eV)	Ion Ratio [b]	Selected Ions for GC-MS
MBT	263 > 207 (5)	263 > 165 (10)	1.05	165, 207, 263
DBT	277 > 221 (5)	277 > 179 (10)	1.41	179, 221, 277
TBT	277 > 221 (5)	277 > 179 (10)	1.38	179, 221, 277
TeBT (IS [c])	291 > 179 (10)	291 > 235 (5)	1.14	179, 235, 291
MPhT	283 > 199 (10)	283 > 241 (5)	1.10	197, 241, 283
DPhT	317 > 275 (10)	317 > 197 (20)	2.01	197, 275, 317
TPhT	351 > 197 (30)	351 > 120 (20)	1.17	120, 197, 351

[a] Collision energy; [b] Peak area of the quantitation trace divided by that of the secondary trace;

[c] Internal Standard.

Table 2. Analytical performance for the determination of OTs by Grignard derivatization and GC-MS/MS.

Compounds	LOD [a] (μgSn kg^{-1})	Linear range (μgSn kg^{-1})	Linearity Coefficient, r^2	Certified value (CE477, mgSn kg^{-1})	Determined value (CE477, mgSn kg^{-1}) [b]
MBT	0.1	0.4-200	0.9996	1.017 ± 0.190	1.133 ± 0.131
DBT	0.1	0.4-200	0.9998	0.790 ± 0.062	0.747 ± 0.048
TBT	0.1	0.4-200	0.9998	0.907 ± 0.078	0.900 ± 0.055
MPhT	0.1	0.4-200	0.9991	-- [c]	0.662 ± 0.080
DPhT	0.05	0.2-200	0.9993	--	0.019 ± 0.001
TPhT	0.1	0.4-200	0.9995	--	0.582 ± 0.013

[a] Limit of detection, for wet sample; [b] n=5; [c] not certified.

Table 3. Detection limits of the proposed method compared to several former reports.

No.	Method	Compounds	LODs (μgSnkg^{-1}, dry weight) [a]	Reference
1	GC-MIP/AES	MBT, DBT, TBT	6.5-14.5	Zabaljauregui etal.[29]
2	GC-AES	MBT, DBT, TBT, MPhT, DPhT, TPhT	0.03-0.30	Delgado etal.[30]
3	GC-PFPD	MBT, DBT, TBT, MPhT, DPhT, TPhT	5.0	Lv etal.[31]
4	LC-MS/MS	TBT	9.1	Zhu etal.[32]
5	GC-MS	MBT, DBT, TBT, MPhT, DPhT, TPhT	4-52	Looser etal.[33]
6	GC-MS/MS	MBT, DBT, TBT, MPhT, DPhT, TPhT	0.01-2.39	Martinez Vidal etal.[27]
7	GC-MS/MS	MBT, DBT, TBT, MPhT, DPhT, TPhT	0.25-0.50	this work

[a] all LODs were converted to the same unit μgSnkg^{-1}, and for comparative purposes, data that were reported on a wet weight basis were uniformly converted to a common dry weight estimate by dividing the wet weight values by five (i.e., 80% water, 20% dry weight tissue) as the report of Araujo etal.[34]

Table 4. Spiked recoveries of OTs in two wet samples (Tonguefishes and Patinopecten yessoensis) and two dry samples (Neverita didyma and Asia Moon Scallop).

Sample	Spiked level ($\mu gSn\ kg^{-1}$)	MBT		DBT		TBT		MPhT		DPhT		TPhT	
		Rec. [a]	RSD [b]	Rec.	RSD	Rec.	RSD	Rec.	RSD	Rec.	RSD	Rec.	RSD
Tonguefishes	4	91.0	2.4	86.0	6.5	76.8	4.7	133.5	1.1	89.8	6.6	70.5	3.0
	20	92.6	8.0	91.8	7.3	92.2	6.8	109.8	2.0	86.3	2.2	95.9	8.1
Patinopecten yessoensis	4	74.5	12.5	82.3	10.7	101.3	4.5	104.3	2.0	78.0	4.5	86.2	5.8
	20	101.5	5.9	95.8	3.5	96.7	1.2	110.4	8.6	88.0	3.6	87.4	7.7
Neverita didyma	20	105.3	6.5	85.8	6.8	97.5	0.5	85.8	5.9	90.3	9.0	94.8	2.6
	100	99.0	5.1	96.8	0.7	89.6	2.6	107.8	6.8	99.8	4.6	104.4	6.2
Asia Moon Scallop	20	92.8	6.4	87.3	5.5	90.2	7.1	97.0	8.2	88.0	6.5	86.3	8.6
	100	87.8	7.1	88.9	8.5	92.8	5.0	82.2	2.7	78.4	2.3	78.8	4.4

[a] average recovery, %, n=3; [b] relative standard deviation, %.

Table 5. Concentrations of OTs in the selected sea products, μgSn kg^{-1}, n=3.

Sample	MBT	DBT	TBT	MPhT	DPhT	TPhT	OTs [a]
Tonguefishes	0.96±0.08	D. [b]	1.65±0.08	N.D. [c]	D.	2.33±0.15	4.94
Acanthogobius hasta-1	1.09±0.12	1.01±0.05	1.94±0.13	N.D.	N.D.	3.26±0.19	7.29
Acanthogobius hasta-2	0.85±0.09	D.	1.59±0.12	D.	0.74±0.03	17.36±1.58	20.54
Mantis shrimp-1	D.	N.D.	1.16±0.09	0.64±0.09	0.39±0.02	2.19±0.12	4.37
Mantis shrimp-2	D.	N.D.	D.	0.94±0.11	1.14±0.08	2.24±0.20	4.33
Octopus	D.	D.	3.51±0.21	N.D.	N.D.	0.88±0.06	4.39
Rapana venosa	D.	D.	D.	N.D.	N.D.	1.36±0.11	1.36
Short necked clam	0.89±0.06	N.D.	1.90±0.18	N.D.	D.	8.88±1.03	11.67
Patinopecten yessoensis	1.09±0.12	N.D.	1.54±0.16	N.D.	N.D.	2.11±0.15	4.74

[a] OTs=MBT+DBT+TBT+MPhT+DPhT+TPhT; [b] detected but not quantified, 3<S/N<10, namely, the detected level >LOD but <LOQ; [c] not detected.

Figure Captions

Figure 1. Elution of propylated butyltin and phenyltin compounds on Silica and Florisil column. The organotin compounds (each 500 ng as Sn) were propylated by n-PrMgBr and extracted with hexane, after concentrated to about 1 mL, the solution was transferred to the pre-activated column (Silica or florisil), then eluted by hexane. Each mL of elution was collected and it was directly injected into the GC for analysis.

Figure 2. Total ion chromatograph (TIC) of propoylated inorganotin and organotin compounds acquired in three scanning modes: A, full scanning; B, selected ion recording (SIR); C, multiple reaction monitoring (MRM). Peak numbers are corresponding to the following compounds: 1-inorganotin, not quantified in this method, 2-MBT, 3-DBT, 4-TBT, 5-TeBT, 6-MPhT, 7-DPhT and 8-TPhT. The Chromatographs were obtained from a shrimp sample. The spiked levels of six OTs were all 100 μgSn kg^{-1}, and the concentration of TeBT (I.S.) was 250 μgSn kg^{-1}.

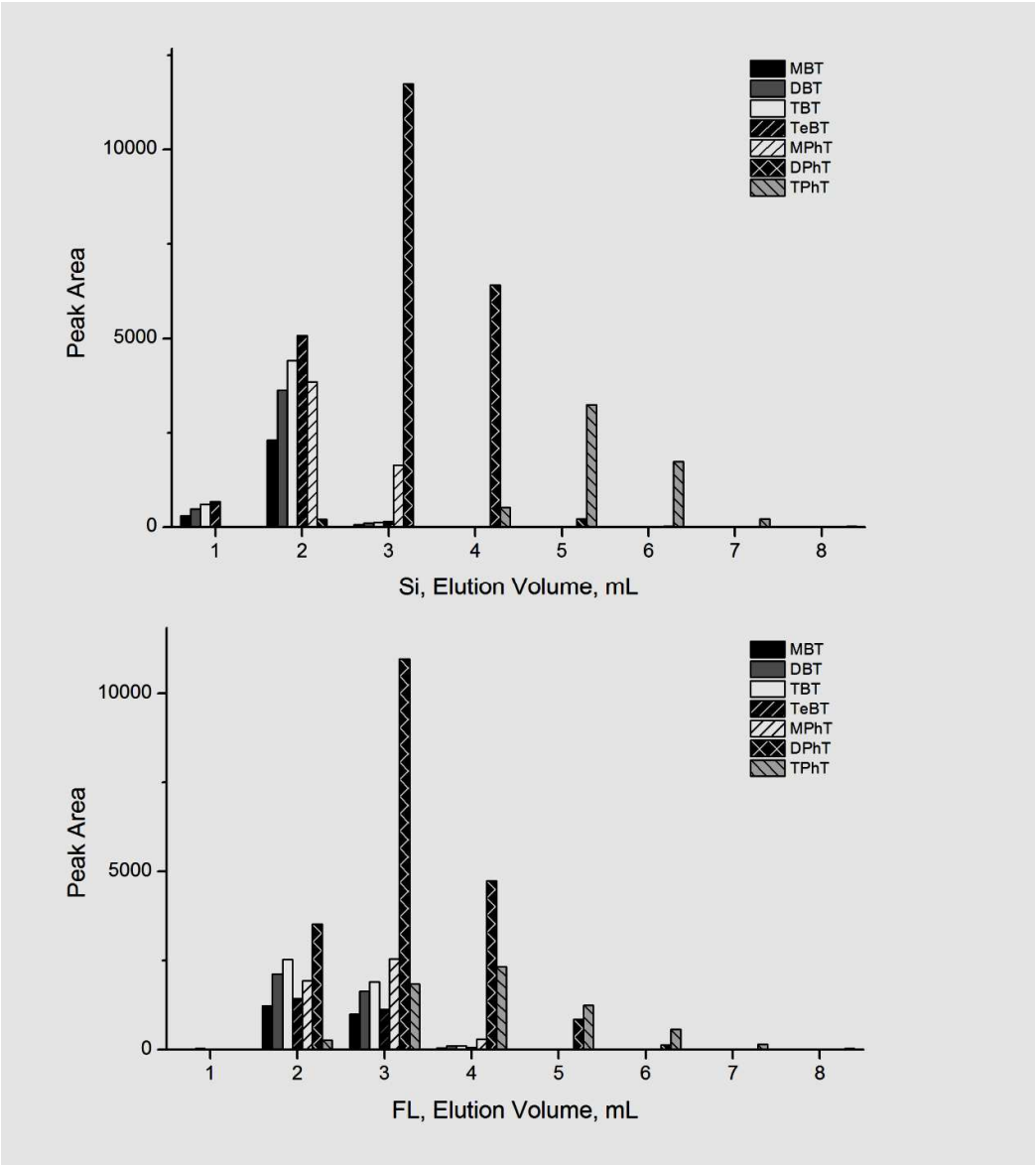

Figure 1

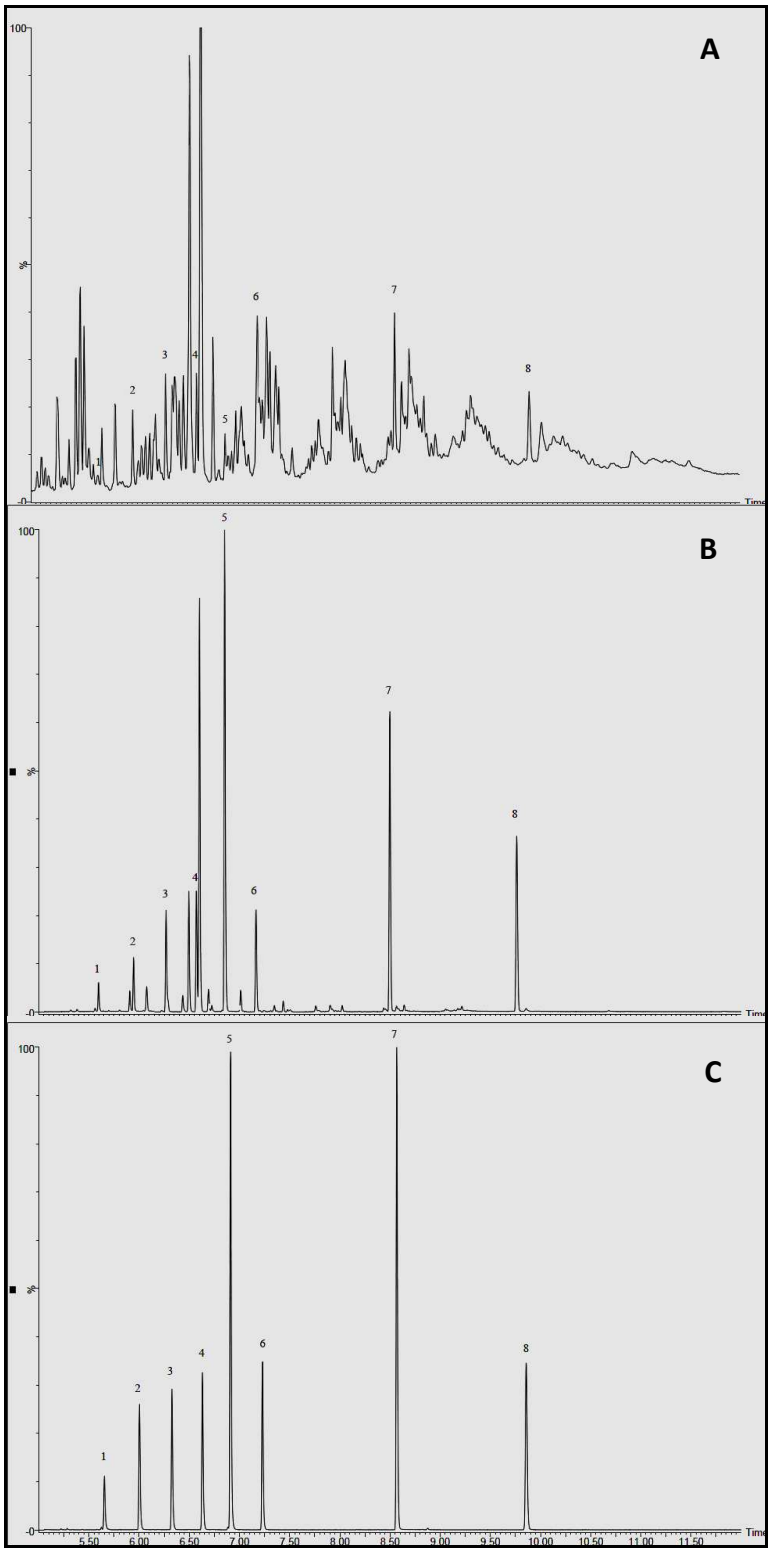

Figure 2.