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High-Speed Survey Method for Photo-degradation Products of Pharmaceuticals Using UV-LED Lighting Device and DART-TOF Mass Spectrometer

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Keywords: PPCPs, Photo-degradation, DART-MS, UV-LED, Pharmaceuticals

Over the past decade, attention as organic pollutants in aquatic environments has been gradually increasing to pharmaceuticals and personal care products (PPCPs). A large amount of pharmaceuticals have been released continuously into aquatic environments for more than a century. Thus, there have been many reports about the occurrence of pharmaceutical products in river water, seawater, and wastewater.

GC-MS and LC-MS or LC-MS/MS are used as the most common techniques for determination of pharmaceuticals in aquatic environments. The selected ion monitoring (SIM), the selected reaction monitoring (SRM) and the multiple reaction monitoring (MRM) methods are utilized as the technique for determination of pharmaceuticals in aquatic environment. When these techniques are used for determination of pharmaceuticals, it is required to obtain the information about the specific ions of target pharmaceuticals prior to starting analyses of them. This indicates that these convenient techniques become useless entirely in determination of unknown compounds.

Photo-degradation is suggested to play an important role in elimination of some of PPCPs from surface waters. In fact, the fate of pharmaceuticals has been recognized by solar and ultraviolet irradiation to them. However, there seems to be also a few reports on the determination of photo-degradation products of pharmaceuticals in aquatic environments in spite of taking a large variety of pharmaceuticals.

Most of investigators have performed the photo-degradation studies by sunlight and/or UV radiation using an appropriately devices equipped with a mercury lamp (Hg-vapor lamp) or a xenon lamp (Xe lamp). The radiation intensity is ca. 300 W/m² (daily average) in the case of solar light¹ and 400-800 W/m² in the cases of Hg-vapor lamp² or Xe lamp³ which consume a relatively long radiation time (about 10 hours) to obtain the significant fate of pharmaceuticals. In addition, these radiation conditions require some cooling system to prevent heat affection. If the photo-degradation study can be performed faster and easier, it will become to assess the photo-degradation products readily. Therefore, we developed the very simple and fast method using a UV-LED lighting device and a DART-TOF mass spectrometer⁴.

A small size UV-LED lighting device has been available recently for UV cure processing on pinpoint. At present time, there are several devices giving ultra violet light (λ max: 365 nm) and high power radiation intensity (to 9500 mW/cm²) with no heat affection. We used the cheap model with radiation intensity of ca. 4000 mW/cm² (40000 W/m²)² and beam diameter of 4 mm (ULEDN-101, NS-Lighting). After preparation of sample solution using methanol and/or acetonitrile (ca. 5 mg/ml), a portion of several micro-L was applied on the reverse-phase type of TLC plate (RP-2 F²₅₄, Merck) using a glass capillary tube and UV light was irradiated for appropriate time (within 120 sec) on the sample spot (diameter: ca. 3 mm). DART-Mass spectrometry was utilized to detect the photo-degradation products on the TLC plate, because the DART ionization provides direct analysis under atmospheric pressure and few fragmentation of molecular ion. In this study, we used DART-SVP100 (IonSence) for ionization of samples and Accu-TOF mass spectrometer (JMS-T100LC, JEOL) for acquisition of mass spectral data.

In this conference, we will present our high advantage method for exploring photo-degradation products of pharmaceuticals by showing the results in the cases of Ibuprofen, Naproxen, Ketoprofen, Indomethacin and Diclofenac which are generally used as a non-steroidal anti-inflammatory drugs (NSAID).

Reference
1) V. Matamoros, et.al., Water Air Soil Pollut., 196, 161-168 (2009)

Novel aspects:
This highest-speed and simplest method will become extremely useful to survey photodegradation products of pharmaceuticals and personal care products (PPCPs) in environment and drug-development research fields.
Ions Observed in DART-MS Analysis of Pharmaceuticals Containing Various Functional Groups on Normal and Reverse Phase TLC Plates

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Keywords: TLC-MS, DART, Pharmaceuticals, PPCPs

Thin Layer Chromatography (TLC) is one of the most popular chromatographic methods and widely used as separation and purification techniques in a variety of fields such as pharmaceutical science, forensic medicine, organic synthetic chemistry, botanical science and environmental analysis. TLC is an inexpensive and easy operation method in comparison to high-performance liquid chromatography (HPLC), gas chromatography (GC) and capillary electrophoresis (CE). However, the identification of compound by TLC analysis often becomes difficult because of its low specificity. To dissolve this problem, mass spectrometry (MS) has been generally used for identification of compounds separated on a TLC plate. In the previous time, the structural elucidation by MS analysis has been carried out after extraction of the target compound from a TLC plate. This off-line TLC-MS method is the relatively much time-consuming technique. Thus, various ionization modes have been investigated to analyze the compounds on TLC plate directly, so far the following ionization techniques have been utilized in a direct sampling TLC-MS analysis; Fast atom bombardment ionization method (FAB), Matrix associated laser desorption ionization method (MALDI), Electrospray ionization method (ESI), Desorption electrospray ionization method (DESI), Direct analysis in real time ionization method (DART), and so on.¹

Among the direct sampling TLC-MS analyses, TLC-DART/MS seems a relatively easy method if a target compound is not non-volatile, because the ionization of compound on a TLC plate can be performed under atmospheric pressure without solvents and matrixes. However, it is relatively difficult and inconvenient to cut a glass type of TLC plate to a narrow width strip (below ca.10mm) after separation of samples on a TLC plate. A new type of DART ion source was introduced in 2009, which allowed the angle of DART gas stream to be adjusted. The new model shall make it easy to access to more wide surfaces compared with the conventional DART ion source (horizontal type).²

On the other hand, the only protonated molecules ions have been discussed in the majority of publications on DART mass spectrometry. In the case of TLC-DART/MS, there are few publications about the detailed investigation on DART mass spectra of compounds containing different functional group.³ Therefore, we started investigation about the characteristics of the DART mass spectrometry to use the TLC-DART/MS method for analysis of pharmaceuticals and personal care products (PPCPs).

At the first time, we selected the typical pharmaceuticals containing various functional groups, which occurred as the major PPCPs in aquatic environments. Most of compounds were obtained by extraction with methanol from the ethical pharmaceutical products, if necessary, were purified by re-dissolving with acetonitrile and/or solid-phase extraction. The silicagel60 F₂₅₄ and RP-2 F₂₅₄ were used as normal-phase and reverse-phase TLC plates, respectively. Both of them were a glass type of TLC plates (20 x 20 cm, stationary-thickness: 0.25 mm) purchased from Merck. The glass strips (100 mm x ca.10 mm) were prepared by cutting TLC plates and washed by development of methanol in a glass developing chamber. After the sample solutions were prepared in a concentration level of 0.1 to 5 mg/mL using appropriate solvent, a portion of 1 or 2 μL was applied on a TLC plate using a glass capillary. DART-MS system consisted of DART-SVP-100 (IonSence) for ionization of samples and Accu-TOF mass spectrometer (JMS-T100LC, JEOL) for acquisition of mass spectral data.

In this conference, we will present the information on DART mass spectrometry of pharmaceuticals spotted on normal- and reverse-phase TLC plates.

Reference

Novel aspects:
This report is the first detailed study on DRAT mass spectrometry of pharmaceuticals containing various functional groups in TLC-DART/MS.
Analysis of thermal products of chlorpyrifos using LC/FTMS

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Keywords: chlorpyrifos, thermal products, LC/FTMS, isomers containing chlorine

Introduction
Chlorpyrifos (O,O-diethylO-3,5,6-trichloropyridin-2-yl phosphorothioate) is an organophosphate insecticide that inhibits acetylcholinesterase and is used to control insect pests. Chlorpyrifos have been used in the lawn on a golf course. It was used for termite control as chlordane alternatives. Sakiyama et al. have reported that 2,3,7,8-TCDD-N-analogue is formed in pyrolysis experiments of chlorpyrifos by GC/HRMS analysis. We should consider carefully burning scrap woods of houses contaminated by chlorpyrifos. It is suggested that the influence appears. In this study, the further thermal products are examined by LC/FTMS and the thermal degradation pathways are proposed.

Methods
All pyrolysis experiments were carried out in sealed brown glass ampoules (10 ml) with about 2 mg of chlorpyrifos and 3,5,6-trichloro-pyridinol (3,5,6-TCP) at temperature between 300 °C and 380 °C. After cooling to room temperature, the ampoules were opened carefully and the reaction products were extracted with toluene. The toluene was concentrated to 1 ml under gentle nitrogen stream. The thermal products of chlorpyrifos and 3,5,6-TCP are analyzed with an Exactive orbitrap mass spectrometer (ThermoFisher Scientific Inc.) equipped with positive electrospray ionization (ESI) probe and Accela LC system (ThermoFisher Scientific Inc.) with a column of Inertsil ODS-3 5um 2.1 × 250mm (GL Science). The best LC separation for the thermal products was achieved using (a) ammonium acetate aqueous solution (5mM) and (b) acetonitrile for the gradient conditions.

Result and discussion
Analysis of chlorpyrifos after thermal treatment at 300 ~ 380 °C was performed by LC/FTMS. The peak intensity of 3,5,6-TCP (m/z= 195.91) was found to increase with decrease in that of chlorpyrifos. The results indicated that the formation of 3,5,6-TCP was probably due to the heating of chlorpyrifos. In addition, the thermal treatment of 3,5,6-TCP showed that the intensity of dimer, trimer, and tetramer ions increased as the peak intensity of 3,5,6-TCP decreased in the mass spectra. The analysis of separation behavior for the LC-MS chromatogram indicated that these polymeric species contained some structural isomers. The new finding obtained from the present LC/FTMS measurements is that the heating of chlorpyrifos generates its oligomers by polymerization. The oligomers are shown to have a wide variety of isomers with different binding sites of chlorine atoms.

1) Sakiyama T, Weber R, Behnisch P, Nakano T, Preliminary Assessment of Dioxin-Like Compounds In/From Chlorpyrifos - A Potential Precursor of the Pyridine Analogue of 2,3,7,8-TCDD, Organohalogen compounds: Vol. 73, 146-149 (2011)

Novel aspects:
The thermal products of chlorpyrifos were identified to be its polymeric species containing a wide variety of structural isomers with different binding sites of chlorine atoms.
Analysis of inadvertent PCBs contained in consumer goods

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Keywords: inadvertent PCB congener yellow pigment

Although production and use of polychlorinated biphenyls (PCBs) were banned in early 70s in Japan, safe storage and disposal of PCBs are still social concern. In addition to that, “irregular” PCB congeners, showing different composition from PCB products, were found unexpectedly in wastewater (1) followed by in air and river water (2, 3), giving rise to another social and technical concern. The origin of such “irregular” congeners has been studied and elucidated (2); they are from polychlorobenzidine dyes and production process thereof and released to the environment finally.

Among 209 PCB congeners, 3,3’-dichlorobiphenyl (PCB 11) and 2,5,2’,5’-tetrachlorobiphenyl (PCB 52) are the most typical inadvertent ones. These congeners in some organic pigments showed different composition profile from the one seen in ordinary PCB products. This means that some portion of PCBs found in the environment may be the byproducts of pigment. Little attention had been paid for them until recently, though US Code of Federal Regulations pointed out the unintentional formation of such byproducts in the yellow pigments in 1979 (4).

Based on such a background, Japanese Government placed an official request for emergency survey of PCB content as for several certain pigments against manufacturers and importers thereof in February 2012 (5). Several consecutive actions have been undertaken so far.

From a point of risk management, it is more important to know the exact congener composition than to know total PCB content, as every congener has its own toxicity varying from the top to the bottom. For such a precise purpose, powerful high resolution GC-MS is preferably used instead of conventional GC-ECD, because GC-ECD, often used for PCB determination in electrical condenser oil, cannot differentiate congener peaks.

Organic pigments have replaced traditional Cadmium Yellow aiming to avoid cadmium, and they are now used for wide variety of industrial products as well as daily consumer goods. It is quite rational to think “Do yellow retail products carry such congeners?” Some analytical results are available in the literature (6), however ordinary consumers may know very little about the material composition of consumer goods. That is why upstream compound maker may have it closed with secrecy reason. Therefore we are somehow anxious about yellow stuff, whether it contains unintentional PCB congeners or not.

Analyses of inadvertent PCBs contained in yellow consumer goods such as crayon, ink, paint, lacquer, adhesive tape and so on were carried out by utilizing capillary GC equipped with high resolution MS in this study. In comparison to the environmental samples such as air and water, sampling itself was easy as for consumer goods. However, it seemed to be difficult to construct typical one standard method so as to cover all samples we dealt. From an experimental viewpoint, clean-up protocol shall be modified case by case according to the property of test sample.

Analytical results obtained are to be presented in this paper.

References
4) 40 Code of Federal Regulations; Environmental Protection Agency: Washington DC, 1979, Part 761.31.(g).

Novel aspects:
Some PCB congeners showing irregular composition profile were found in some pigments, and becoming social concern. Analyses of inadvertent PCBs contained in consumer goods were carried out.
Suspended solid as a disturbance of PFOS analysis in case of wastewater

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Keywords: PFOS SS surrogate recovery COP4

Perfluorooctane Sulfonate (PFOS) is one of the Perfluoroalkane Sulfonates (PFASs) and is also the terminal degradation product of many perfluoroalkyl compounds (PFCs). Specific properties of PFCs such as water repellency, thermal stability, and surface tension lowering, made these compounds important both for commercial and technical aspects.

As a consequence, PFOS having several emission paths to the environment had been broadly spread out over 50 years. Recently PFOS was designated and restricted as persistent organic compounds (POPs) by the Stockholm Convention on POPs (1).

In Japan, PFOS was specified to the first class chemical under the Chemical Substance Control Law followed by filing technical guideline for disposal of PFOS containing garbage in March 2011 (2). Several kinds of standard analytical method using LC-MS/MS (2-4) had been proposed for surface water prior to that.

Many papers pointed out the technical difficulties arising from the contamination owing to flurine resin used for connectors or tubing material in the apparatus, even when clean water was analyzed (5).

Other than contamination, we encountered different difficulties when we applied current analytical methods to the wastewater in the beginning of our study. We experienced low recovery of surrogate substance that was added to the sample to ensure the precision. Low surrogate recovery did not meet the requirements prescribed in the current analytical standards designed for surface water.

We found the reason for the difficulties. On one hand, it is known among the lab analysts that concentration of PFOS is prone to be decreased probably owing to the adsorption toward labware. But on the other hand, little attention was paid for the adsorption onto suspended solid (SS) in case of surface water, in spite of numerous efforts to develop sampling and analytical methods for PFOS, since SS content in surface water is generally enough low (6).

Development of harmless disposal method undergoes, analysis of wastewater we concern shall be required. Proper care should be taken for adsorption on SS for the analysis of water containing high SS.

Among elution conditions of PFOS, eluent composition was intensively investigated, and in addition we found both quality and quantity of SS affected on surrogate recovery, leading to an improvement toward current method. We would suggest the importance of SS remained on the filter upon analytical results.

The last portion of this study relates to the effect of perfluoroalkane chain length on the recovery, and results are to be discussed.

Acknowledgements
The authors thank Mr. Shusuke Takemine of Hyogo Prefectural Institute of Environmental Sciences for helpful discussions about PFOS nature.

References

Novel aspects:
Recovery of surrogate substance in PFOS analysis was investigated to improve current method, and the effect of chain length of perfluorinatedalkane on the recovery is to be discussed.
Dechlorane Plus, a highly chlorinated flame retardant in Japanese environment samples.

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Keywords: Dechlorane Plus, Japan, Environment

Dechlorane Plus (DP) is a highly chlorinated flame retardant, was developed to replace Mirex (Dechlorane) that was banned in the 1970s. It is manufactured about 450 ton per year by Occidental Chemical Corporation (OxyChem) in the United States. In 2006, the first of sightings of this chlorinated flame retardant were in the Great Lakes region, and the investigation reports are increasing rapidly recently in the world, mainly in North America. More recently, a newly DP production facility was discovered in China. It is estimated that Chinese capacity of DP production has reached 2,000 ton in 2006.

However, to our knowledge, no data for levels of DP in environmental samples were available in Japan. Therefore, we measured DP by using the GC / high resolution MS in EI mode, and identified this compound in the environmental samples collected from Japanese urban area. DP was detected in house dust, deposit of the window frame, road sediment, garden soil and sediment samples at concentrations ranging from 2.9-42ng/g-dry, 240-270ng/g-dry, 74-150ng/g-dry, 1.7ng/g-dry, 17-140ng/g-dry, respectively. Further, we showed the mean of anti-DP fractional abundance ($f_{\text{anti}}$) value in these Japanese samples was 0.65, 0.83, 0.80, 0.81, 0.81, respectively. This compound had not been identified in the environment of Japan before our report. In this conference, we will indicate the detailed additional data of DP in surface sediment samples of the urban river in Japan.

Novel aspects:
Dechlorane Plus was determined in environment samples for the first time in Japan.
Level of Dechlorane Plus in ambient air and development of monitoring method

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Keywords: Dechlorane Plus, ambient air, NCI

A chlorinated flame retardant, Dechlorane Plus (DP) (syn-, anti-), was detected and identified in ambient air from Japanese urban area. This study shows that DP was detected in air samples in Japan for the first time. In a moment of this research, we investigated the mode of ionization using GC/MS availability. GC/MS is commonly applying to determine DP with negative chemical ionization (NCI) mode at low resolution (LR). DP was also determined magnetic sector-type MS with electron impact ionization (EI) mode at high resolution (HR). R^2 for calibration curves on DP (syn-, anti-) were over 0.9999 of LR-NCI and HR-EI method. Instrument Detection Limits (IDL) of both methods for DP (syn-, anti-) were 0.20 pg/m^3, 0.23 pg/m^3 and 0.34 pg/m^3, 0.36 pg/m^3 respectively. LR-NCI method was S/N = 50 at 0.1 ng/mL standard solution that approximately four times greater than HR-EI method. Result of compared both methods, LR-NCI method was applying in this study.

Air samples were collected on the rooftop of Japan Environmental Sanitation Center. Samples were collected 24 hours and repeated 4 times. All samplings were implemented duplicate. Result of measurement by GC/MS (LR-NCI), DP air concentration ranged from 1.9 to 21 pg/m^3. Recoveries of ^13C labeled DP were more than 90%. The syn- and anti- ratio were read between 0.24 and 0.48. All duplicates were considerably fit in each sample. DP concentrations were higher than Mirex to compare with Environmental Survey and Monitoring of Chemicals was implemented by Ministry of the Environment Japan.

Novel aspects:
Dechlorane plus were determined in air samples for the first time in Japan.
Determination of hydroxylated polycyclic aromatic hydrocarbons in mariner’s urine by high performance liquid chromatography-tandem mass spectrometry

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Keywords: Polycyclic aromatic hydrocarbons, Urine, Human exposure, LC/MS/MS, metabolite

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals released into the air during the incomplete burning of fossil fuels such as gasoline and other organic substances. Some PAHs are reasonable anticipated to be human carcinogens. The carcinogenic risk to humans among 16 PAHs is classified as probable human carcinogens by the International Agency of Research on Cancer in 2010. PAHs are also known to have endocrine disrupting activity. PAHs are absorbed into the human body through the skin, lungs and gastrointestinal tract and are then metabolized to their hydroxylated PAHs (OHPAHs) and finally excreted in urine. In this study, a high performance liquid chromatography-tandem mass spectrometry method has been developed for the simultaneous quantification of six urinary OHPAHs, including 1-hydroxynaphthalene (1-OHNap), 2-hydroxynaphthalene (2-OHNap), 1-hydroxyphenanthrene (1-OHPhe), 3-hydroxyphenanthrene (3-OHPhe), 4-hydroxyphenanthrene (4-OHPhe) and 1-hydroxypyrene (1-OHPyr) in human urine. Deuterated 3-OHPhe-d9 and 1-OHPyr-d9 were used for the quantification of the analyte as internal standards. Considerable amounts of PAHs are present in the workplace. PAHs exposure is reported high in coke plants, aluminium work and paving work. In order to assess the potential health risks posed by exhaust gas from ship and obtain a better understanding of the occupational hazards connected with PAHs exposure, the concentration of OHPAHs in urine collected from mariners has been analyzed.

The urine sample treatment involved enzymatic hydrolysis of glucuronide and sulfate conjugates followed by solid-phase extraction using Sep-Pak C₁₈ cartridge for LC/MS/MS analysis. The LC/MS/MS system consisted of an Agilent 1260 infinity series (Agilent Technologies, Santa Clara, CA, USA) and QTRP 5500 mass spectrometer (AB SCIEX, Framingham, MA, USA). The analyte and ISTD were separated from interference peaks on an Ascentis Express C₁₈ column (2.1mmID × 100mm, 2.7 μm particle size; SIGMA-ALDRICH Co., St. Louis, MO, USA). The mass spectrometer was operated under multiple reaction monitoring (MRM) negative mode for the ion transitions m/z 143 → 115 (OHNap), m/z 193 → 193 (OHPhe), m/z 202 → 202 (OHPhe-d9), m/z 217 → 189 (OHPyr) and m/z 226 → 198 (OHPyr-d9).

This method was applied to the analysis of OH-PAHs in 29 urine specimens (11 engineers and 18 other crews) collected from the crews on a ship. The average concentrations of urinary 1-OHNap, 2-OHNap, 1-OHPhe, 3-OHPhe, 4-OHPhe and 1-OHPyr were 1.6, 2.2, 0.2, 0.2, 0.1 and 0.2 μg/g creatinine in engineers and 0.5, 1.8, 0.2, 0.1, 0.1 and 0.1 μg/g creatinine in other crews, respectively. The method can be used to evaluate occupational exposure to PAHs.

Novel aspects:

We assess the potential health risks posed by exhaust gas from ship and obtain a better understanding of the occupational hazards connected with PAHs exposure.
Analysis of perfluorinated compounds in sediment samples from wastewater canal of Pancevo industrial area, Serbia

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Keywords: PFOA, PFOS, Industrial wastewater canal, Sediment, Danube River

Perfluorinated compounds (PFCs) are chemicals that do not occur naturally, but have been widely used in chemical production for some time. They are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful. Perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the two PFCs most commonly used and found in the environment. Together with perfluorohexane sulfonate (PFHxS) these compounds are widely employed in different industrial processes such as in protective coatings.

The wastewater canal (WWC) Vojlovica was built in 1962 to collect the wastewater discharges from the industrial complex of the city of Pancevo in Serbia. Industrial complex consist of a petrochemical factory (HIP Petrohemija), an oil refinery (NIS Rafinerija, Pancevo) and chemical fertilizers factory (HIP Azotara). The canal is artificial with no natural flows, about 2 km long, around 70 m wide and directly connected to the Danube River. The water depth is around 12 m. The environment surrounding the canal has been strongly affected for a long time by the presence of the industrial complex. Additionally heavy destruction during NATO bombing events in 1999 resulted in contamination of air, soil, groundwater and the WWC itself.

In total, 4 sediment samples from WWC were collected. Surface sediments layer of 15 cm were taken by a Van Veen Grab sampler, transported in glass jars and stored in the laboratory at 4°C. For comparative purposes, the same type of sample were also taken from the navigation canal flowing parallel to WWC but not receiving any direct discharge of industrial wastewaters.

Sampling sites are listed below:
No1 - navigation canal;
No2 - at the confluence of WWC with the Danube River, downstream from the industrial area and effluents;
No3 - downstream from the fertilizer factory outlet (first effluent);
No4 - downstream from the petrochemical plant (second effluent);
No5 - downstream from the oil refinery outlet (third effluent).

Sediment sample was extracted with methanol. MPFAC-MXA as mass-labeled surrogates was spiked into the sample. The sample was extracted with SPE. The elution was concentrated and labeled $^{13}$C₈PFOA was added as syringe spike. The each final solution was analyzed by liquid chromatography (LC)-tandem mass spectrometer (MS/MS) using Xevo TQ (Waters) coupled with ACQUITY UPLC (Waters).

Concentrations of PFCs were determined as follows:
No1: 68, 230 and 230 ng/kg-dry of PFOA, PFHxS and PFOS, respectively.
No2: 80 and 2100 ng/kg-dry of PFOA and PFOS, respectively.
No3: 170 and 5300 ng/kg-dry of PFHxS and PFOS, respectively.
No4: 130, 170, and 5700 ng/kg-dry of PFOA, PFHxA, and PFOS, respectively.
No5: 76, 66 and 420 ng/kg-dry of PFOA,PFHxA, and PFOS, respectively.

Concentrations of PFOS in the samples No3 and No4 are 3-3.2 times higher compared with sea sediment in Tokyo bay ¹. PFOA and PFOS concentrations from WWC were from two to twenty fold higher comparing to sediment samples taken from Roter Main river (Germany) which receives treated waste waters of industrial, commercial and domestic origin from municipal wastewater treatment plant ². Comparing to upstream Danube River bank sediment samples ³ PFOS from the WWC samples were from two to six fold higher.

This is the first study and report of presence of PFCs compounds in the samples from Serbia. Most of the PFCs are released from fertilizer factory and petrochemical plant outlets, while oil refinery outlet mostly contribute to petroleum pollution. The exact origin of PFCs cannot be established from one study but one of the reasons for presence of these compounds might be their usage as components in pipes, fittings and wiring insulations.

¹) Zushi Y. et al Environmental pollution 158, 756-763 (2010)
²) Becker, A.M et al Environmental Pollution 156, 818-820(2008)
Novel aspects:
This is the first report of presence of PFCs compounds in the sediments from Serbia. Compared to other reports, high levels of PFOA and PFOS were found.
Adosorption property of PCB 209 congeners by gamma-cyclodextrin polymer

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Keywords: Atropisomer,Congener specific analysis,GC-MS/MS,PCBs and other toxic substances,Persistent Organic Pollutants(POPs)

Polychlorinated biphenyls (PCBs) production in Japan was started by Kaneka Chemical in 1954. The infamous incident of Yusho, rice-oil poisoning, took place in western Japan in 1968. In 1970’s, regulations over PCBs production and use became enforced and PCBs disposal measures have been in operation since 1980’s. PCBs waste destruction is still going on today. PCBs were widely used as insulating fluids in capacitors and transformers. Although their manufacture and commercial use have been prohibited in many countries since the 1970s because of their strong toxicity, environmental persistence, and bioaccumulation, large amounts of insulating oils contaminated with PCBs are still being used or are kept without being appropriately treated in many countries, including Japan. In the Stockholm Convention on Persistent Organic Pollutants (POPs), more than 150 countries have agreed to destroy PCBs until 2025. Thus, the efficient and safe treatment of PCB-contaminated insulating oils is a crucial problem from a global viewpoint.

Cyclodextrins (CDs) are a class of cyclic oligosaccharides consisting of several gamma-(1,4)-linked D-glucopyranose units. They have a hydrophobic cavity into which a guest molecule of an appropriate size and shape can be incorporated. The ability of CDs to form inclusion complexes with organic molecules has found applications in many areas, including the food and pharmaceutical industries and analytical chemistry. However, in most cases, inclusion complex formation with CDs has been achieved in aqueous media. On the other hand, much less attention has been paid to inclusion complex formation with CDs in nonpolar organic media, because it has been believed that inclusion complex formation in nonpolar organic media would be very difficult due to the unfavorable competition with enormous amount of nonpolar organic solvents against the guest molecules for inclusion into the CD cavity.

We were reported here the removal of PCBs from insulating oil or nonpolar organic solvents by gamma-CD polymers as a new adsorbent. Nonpolar organic solvents containing PCBs and other toxic substances were analyzed adsorption character which passed gamma-CD polymers solid phase using the GC-MS/MS. PCB 209 congeners were analyzed by product ion obtained by destroying precursor ion using MS/MS method. Other toxic substances were analyzed in the same way. The gamma-CD polymers were prepared by the reaction of gamma-CD with various kinds of crosslinkers. Among the gamma-CD polymers thus obtained, the polymer crosslinked with terephthaloyl units showed the highest adsorption capability towards PCBs. Using this type of polymer (more than 45 wt% of insulating oil or nonpolar organic solvents) as an adsorbent, PCB 209 congeners and other toxic substance, whose initial concentrations were 1~100 ppm, were completely removed from isooctane solution.

Novel aspects:
Nonpolar organic solvents containing PCBs and other toxic substances which passed gamma-CD polymers solid phase were analyzed congrener-specifically using the GC-MS/MS.
This analytical method is suitable for the determination of Hydroxylated Polychlorinated Biphenyls (OH-PCBs) in ambient air by gas chromatography- high-resolution mass spectrometer with selected-ion monitoring (GC/HRMS-SIM). OH-PCBs are considered as one of the endocrine disturbing chemicals because OH-PCBs have negative impacts on the some thyroid and female hormones. OH-PCBs are formed by metabolism of PCBs by the cytochrome P450 enzyme-mediated oxidation and OH radical reaction of PCBs. The concentrations of OH-PCBs in the environmental waters, air, sediments and living things have been investigated and OH-PCBs have been detected from every medium. In Canada, OH-PCBs were also detected from the rain and snow. In this study, we modified the analytical method and investigated the concentration of OH-PCBs in ambient air. The air was introduced into quartz fiber filter (QFF) and poly urethane foam (PUF) which were set to Hi-Volume air sampler at a flow rate of 700 L/min for 24 hr (total volume was 1000 m$^3$). After collection was completed, clean-up spike (OH-Di-Hp-CB-13$^{13}$C$_{12}$ 3.0ng) was added to the PUF. Both QFF and PUF were simultaneously extracted with acetone by ASE. The acetone extract was added 6 mL of 5% sodium chloride solution, and extracted with 2 mL of hexane, twice. The hexane phase was clean upped with pre-washed Sep-Pak Plus Florisil. Sep-Pak Plus Florisil was eluted with 0.5% diethyl ether/hexane 8 mL (for PCB), and then with 50% acetone/methanol 10 mL (for OH-PCBs). The eluate was concentrated until just before dryness. After derivatization and alkaline digestion, added 6 mL of 5% sodium chloride solution, and extracted with 2 mL of hexane, twice. Concentrated to about 1 mL and dehydrated with anhydrous sodium sulfate. The concentrate was applied to a pre-washed Sep-Pak Plus Florisil, and eluted with 8 mL of 5% diethyl ether/hexane. The eluate was concentrated to 100 μL and added syringe spike (MBP-70$^{13}$C$_{12}$ 0.50 ng). The method detection limits (MDL) and the method quantification limit (MQL) were 0.067 - 0.13 and 0.17 - 0.33 pg/m$^3$, respectively. The average of recoveries (n = 3) from 1000 m$^3$ of air sample added with 3.0ng OH-PCBs were almost 60-110%, and the relative standard division was 1.2 - 24%. Lowly chlorinated OH-PCBs tend to be collected in PUF and highly ones tend to be collected in QFF. In the air samples, OH-PCBs were detected 1pg/m$^3$ order and the lowly chlorinated OH-PCBs were dominant.

**Novel aspects:**
OH-PCBs in ambient air was detected using QFF and PUF which were set to Hi-Volume air sampler.
No.100532

Application of HPLC/MS in determination of heroin metabolites in saliva an urine samples

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Keywords: saliva; urine; heroin; metabolite; glucuronide

Introduction
Urine is a common, and saliva represents an alternative specimen for substances of abuse determination in toxicology. In this study, one step was to optimize a method for saliva and urine specimen preparation for heroin metabolites, codeine, 6-monooacetylmorphine (6-mam) and morphine determination by high performance liquid chromatography-mass spectrometry (HPLC/MS), and then this method was applied on saliva and urine samples taken from the patients. As a preliminary analysis, test strips for opiates identification in patients’ urine were used. Saliva and urine samples from patients whose preliminary test was “positive” were taken for further analysis.

Methods
Sample preparation
Both, saliva and urine specimens was prepared using liquid/liquid extraction of codeine, 6-mam and morphine by mixture of chloroform and isopropanol (9:1; v/v).

HPLC/MS analysis
Extracts were analyzed by HPLC-ESI-MS technique: at Waters Alliance system, the separation column Waters Spherisorb 5 μm, ODS2, 4.6 × 100 mm was used; mobile phase: ammonium acetate : acetonitrile (80:20; v/v), mobile phase flow rate 0.3 mL/min, autosampler temperature 20 °C; injection volume 50 μL; Mass detection range: 100–400 m/z, centroid mode, interscan delay 0.1 s, scantime0.5 s, splitless, four voltage values: 70, 60, 50 i 38 V, ES+, source temperature 150 °C, desolvation temperature 430 °C, gas flow for desolvation 362 L/h and at cone 135 L/h, capillary voltage 3 kV - mass spectrometer Waters Micromass ZQ™ (Waters Corporation, Milford, MA, USA).

Calibration and optimization were done using morphine standard (ion 286) 10 mg/L at flow rate 10 mL/min. Regression and correlation analyses were performed with the probability level of 0.05. Mass spectra were analyzed by software Waters MassLynx™ (Waters Corporation, Milford, MA, USA).

Results and Discussion
Calibrations for each analyzed substance in both specimens were done in the concentration range from 0.1 to 1 mg/L and the coefficients of correlation were above 0.99. Recoveries for morphine and codeine determination in saliva was 99%, while for 6-mam it was 94% and recoveries for morphine, codeine and 6-mam for determination in urine were 103%, 101% and 93%, respectively. Limits of detection and quantification of a proposed method were 0.01 mg/L and 0.05 mg/L, respectively for both sample types.

Applying the proposed method on real samples of patients (n=10) where positive reaction was obtained on test strips we determined concentrations of heroin metabolites in selected samples in following ranges: Concentration of codeine in the saliva of the heroin abusers ranged from 0.05 to 5.33, for morphine between 0.05 and 5.33 and for 6-mam between 0.01 and 0.68 mg/L. Concentration of codeine in the urine samples of the same patients ranged from 0.22 to 5.74, for morphine between 0.15 and 6.32 and for 6-mam between 0.05 and 1.78 mg/L.

A proposed HPLC/MS method for codeine, 6-mam and morphine determination in saliva and urine samples is accurate, simple, cheap and suitable for routine analysis and monitoring of heroin abuse.

Novel aspects:
Developing accurate, simple, cheap and suitable method in determination of heroin metabolites in saliva an urine with HPLC/MS
Information of the behavior of the persistent organic pollutants in the sea around Japan

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Keywords: POPs, HCHs, enantioselective analysis, Japan Sea

Although a large amount of Persistent Organic Pollutants (POPs) have been used in Asian countries such as China or Korea, the state of contamination has not been clarified in Japan Sea surrounded by these countries. In this study, pollution levels of POPs in sea water and air over the ocean were investigated by using voluntary sampling of passenger ships. Also isomer and enantiomer analysis were conducted to estimate the source and pollutant pathway of POPs.

The sea water samples (approx. 50L) and air samples(approx.108m^3) were taken by the passenger ship (NYK crusies CO., LTD, ASKA-2) equipped with concentrating device between 2009 and 2011. Also in downstream site of Chang Jiang, water samples(approx.6L) were taken in 2010 and 2011.

Identification and quantification of POPs were performed using a gas chromatograph, (HP6890N Agilent) /high-resolution mass spectrometer(800D,JEOL Ltd.) equipped with HT-8PCB capillary column (60m*0.25mm id,Kanto Chemical) and BGB172 capillary column(30m*0.25mm id,BGB Analytik AG) for enantioselective analysis

In this result, the highest concentration of Hexachlorocyclohexanes (HCHs) was in the sea around the northern Hokkaido, 880pg/L. DDTs was higher in Tsushima straits than in the north of Japan Sea. On the other hand, it is several times higher concentration in Chang Jiang than in around the Sea of Japan, 1300~2600pg/L (HCH).

From the view point of isomer pattern, the ratios (α/γ) of Sea waters were apparently different according to the areas. In general, lower α/γ ratios were observed in low-latitude region. Especially in downstream site of Chang Jiang, it was the lowest value,1.4±0.1, and 1.9±0.6 in the seas around Korea, 4.2~0.6 in southwestern Sakhalin. These results seem to reflect the usage of γ-HCH(Lindane) in China and indicate that HCHs was discharged to the marginal seas of the region through rivers in considerable amounts and transported to Japan Sea via oceans.

Dechlorane Plus (DP) is a chlorinated FR additive introduced as a replacement for Dechlorane, or Mirex. In the past, there are few data of DP in the environment. In this study the concentration of DP in the sea water was investigated for the first time. The range of DP is 0.7~14pg/L in the sea around Japan and 5~16pg/L in Chang Jiang.

As for chiral analysis, it is regarded that enantioenrichment indicates that it was released some time ago and has since been subjected to recycling from water or soil. EF value of α-HCH was close to racemic in southwest Sakhalin(0.5~0.02) , downstream site of Chang Jiang (0.51~0.02) . In Chang Jiang and the northern Hokkaido, enantiomer fractions (EFs) of alpha-HCH was nearly 0.5(racemic). It suggests that those areas were affected by relatively-recent pollutant source.

In Japan Sea, as latitude become higher, EF values tend to become lower. Since 2005’s survey , EF values was 0.46~0.05 in middle Japan Sea, 0.44~0.03 in northern Japan Sea(around Hokkaido),0.46~0.01(pacific sideboard of Tohoku area). These results indicate that southwest Sakhalin, downstream site of Chang Jiang and Tsushima Straits area polluted by relatively new HCHs.

From comprehensive viewpoint, there is a possibility of contamination in Japan Sea, which is caused by the transportation from other countries and polluted area by HCH was found in around Hokkaido.

Novel aspects:
Pollution levels of POPs in sea water and air over the ocean were investigated. Also isomer and enantiomer analysis were conducted to estimate the source and pollutant pathway of POPs.
Identification of chlorinated aromatics as impurity of chlorinated paraffins by GC-HRMS or GC-HR-Tof-MS

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Keywords: POPs, Chlorinated Paraffins, Impurities, Identification, PCB

Chlorinated paraffins (CPs) are industrial products used as metal-working fluids and flame retardants for plastic materials. Short chain CPs (SCCPs) seems to persist in the environment and bioaccumulate in biota, and are under review by the Stockholm Convention on persistent organic pollutants.

We identified high levels of POPs such as PCBs, PCBz, PCNs and HCHs from air sampler materials. After detailed investigations these POPs are concluded as impurities of technical chlorinated paraffins (CPs), which used for rubber materials as flame retardant at 2-6 % contents. The exact mass spectrum and accurate mass of these chemicals are fixed theoretical mass with few ppm errors. The profile of PCBs congeners are close to technical PCBs, which suggest chlorination of biphenyls as impurities of paraffins. The homologue profiles of PCBs are relatively lower chlorination pattern with some specific congeners.

These technical CPs are imported from China. The production of total CPs in China has continued to increase, reaching 600,000 tones in 2007. Although the huge production and use of CPs in China could imply potential contamination of various media, there is little information on exposure to SCCPs. In our previous study, the analytical methods for SCCP were investigated in detail and applied for dietary samples. Preliminary evidence on the significant increase of SCCP in food sample Beijing in 2009 warrants urgent investigations to refine dietary intake estimates by targeting food types and source identification.

On the other hand, the finding high levels of legacy POPs as impurities in technical CPs are more serious for POPs inventories around the world.

Novel aspects:

Identified high levels of POPs in technical CPs and products by GC-HRMS or GC-HR-Tof-MS