



Polymeric ion exchange material based dispersive micro solid-phase extraction of lipophilic marine toxins in seawater followed by the Q Exactive mass spectrometer analysis using a scheduled high resolution parallel reaction monitoring

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ABSTRACT

In recent years, harmful algal blooms have been occurring frequently all over the world, which caused a great negative impact on marine ecosystem, aquaculture and human health. Lipophilic marine toxins (LMTs) produced by certain harmful alga are closely related to diarrhetic shellfish poisoning. In this study, a new sample preparation method was established by performing dispersive micro solid-phase extraction (DMSPE) procedure using mixed polymeric ion exchange material as the adsorbent for the simultaneous extraction of LMTs in seawater. To obtain the optimal extraction efficiency of LMTs, the key factors including the type and the amount of adsorbent, the type and volume of eluent, and the concentration of sodium chloride were investigated in detail. A good enrichment effect and weak matrix effects were observed after the DMSPE procedure. Compared with conventional solid-phase extraction sample preparation, the advantages of DMSPE procedure were present in convenience and low cost. In high resolution mass spectrometry (HRMS) detection, a new scheduled high resolution parallel reaction monitoring (PRM) mode was selected for qualitative and quantitative analysis to improve the selectivity and sensitivity of LMTs in seawater. Based on an effective combination of DMSPE procedure in sample preparation and high resolution PRM in data acquisition, a sufficiently low detection level (pg/L level) was achieved for the routine monitoring of LMTs in seawater.

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1. Introduction

In recent years, the phenomenon of algal blooms all over the world has gradually increased due to an excessive supply of nutrients [1,2]. Some marine microalgae can produce harmful algal toxins that can be further accumulated in shellfish via the food chain. Lipophilic marine toxins (LMTs), about 90% of all known marine toxins, are widely distributed around the world, which has become a serious threat to marine ecological environment, public health and quality assurance of shellfish products [3]. With the increasing concern for LMTs in shellfish products, more and more researches have been oriented towards the trace analysis and monitoring of LMTs in marine ecological environment. Several studies have reported the existence of multiple LMTs in seawater from

Belgium, France, Qatar, North-central Adriatic Sea and China [4–11]. These LMTs mainly include azaspiracids (AZAs), okadaic acid (OA), dinophysistoxins (DTXs), anatoxin a (ATX-a), gymnodimine (GYM) and 13-desmethyl spirolide C (SPX1), shown in Fig. 1. Due to their very low concentration level (ng/L or pg/L) in seawater, it is very important to establish a highly sensitive and simple analytical method for routine monitoring.

In view of the trace analysis of LMTs in seawater, enrichment effect of sample preparation directly affects the method sensitivity. The most widely used sample preparation technique in the existing analytical methods is solid-phase extraction (SPE) column or disk [12–16]. This technique presents high cleanup and pre-concentration capabilities, but one of its biggest drawbacks is that a certain back pressure can be created when a large volume of seawater is loaded in column, so the procedure often needs to be controlled by additional equipments with a tedious and time-consuming operation. Meanwhile, the cost of existing commercialized SPE column or SPE disk was relatively high. In preliminary studies, due to weak alkaline characteristics of ATX-a, AZAs, SPX1 and GYM, a better adsorption effect was observed in strong

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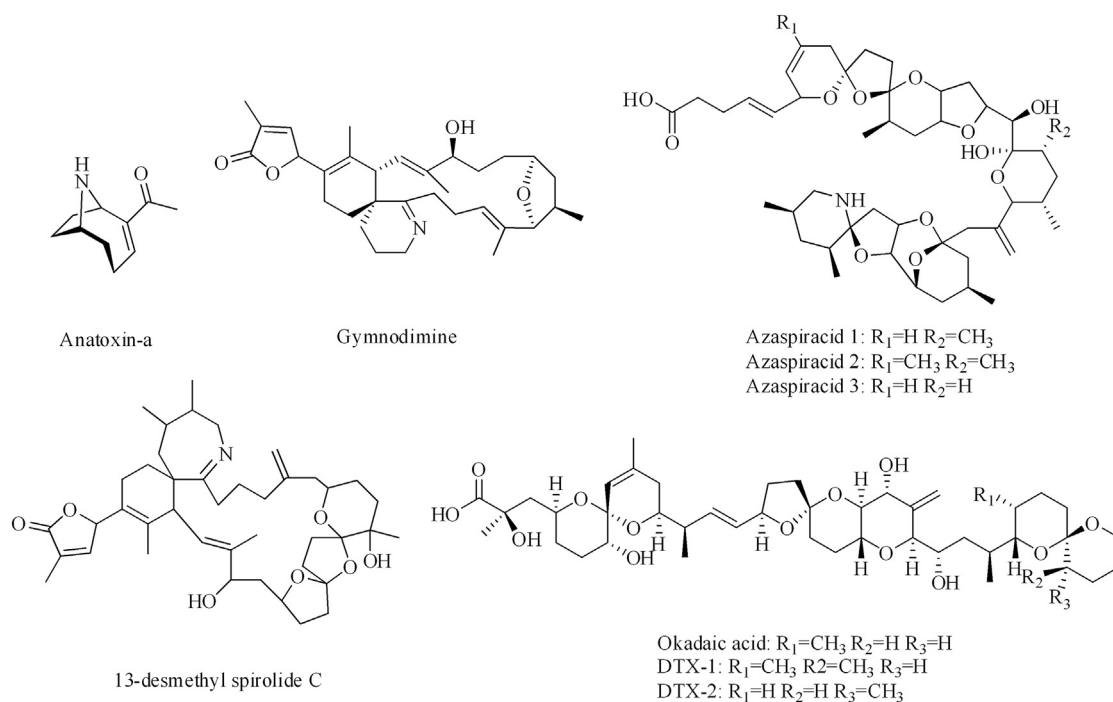


Fig. 1. Molecular structures of lipophilic marine toxins.

cation-exchange SPE column than in hydrophilic lipophilic balance (HLB) column, while acidic LMTs (OA and DTXs) were suitable to be adsorbed in strong anion-exchange SPE column. In order for the simultaneous analysis of these LMTs with optimal effects, it often requires two SPE columns to be used. Dispersive micro solid-phase extraction (DMSPE), a miniaturization model of SPE based on using a small amount of solid sorbent, was proven to be a simple and rapid technique for effective cleanup [17]. For DMSPE technique, the solid sorbent is added directly to the extracts, and the procedure relies only on shaking in a short time. This makes sample pretreatment simpler, more inexpensive and time-saving compared with traditional SPE. Moreover, an additional advantage of this technique is that the suitable mixed adsorbents can be selected according to the individual properties of the analytes. Due to its excellent advantages, DMSPE has gained an increasing popularity in the analysis of environmental, food, pharmaceutical and biological samples [18–23]. Nonetheless, there is still no report on the application of DMSPE procedure using mixed adsorbents. In this study, PCX and PAX, as strong cationic and anionic exchange polymeric material, respectively, were used as the mixed adsorbents of DMSPE to the extraction of LMTs in seawater.

In trace analysis of LMTs, liquid chromatography-tandem mass spectrometry (LC-MS/MS) using multiple reaction monitoring (MRM) mode is still the most commonly used detection technique [11–14]. Recently, researches have been launched on the use of high-resolution mass spectrometry (HRMS) technique to reduce the complex optimization procedure of acquisition parameters and benefit from the advantages of the higher specificity and qualitative ability with more detailed structural information [4,24,25]. In quantitative analysis, full scan, as a widely-used acquisition mode in HRMS, cannot achieve superior sensitivity compared with the MRM mode in tandem mass spectrometry. Fortunately, parallel reaction monitoring (PRM) mode, previously described as targeted MS/MS (tMSMS) in Q Exactive HRMS, is similar to the MRM mode in tandem mass spectrometry [26–28]. By PRM analysis, a MS scanning point covers all fragment ions with accurate mass for a target compound, thus greatly improving the qualitative and quantitative capabilities. In this study, a new analytical method was established to the simultaneous analysis of LMTs in seawater based on an effective

combination of DMSPE procedure in sample preparation and high resolution PRM in detection analysis.

2. Materials and methods

2.1. Chemicals and materials

Acetonitrile (MeCN), methanol (MeOH), formic acid, ammonium formate and ammonium hydroxide were of HPLC grade and obtained from Fisher Scientific (Fair Lawn, NJ, USA) and Tedia (Weston, OH, USA). Ultra-pure water was prepared on a Milli-Q Plus system (Bedford, MA, USA). PCX, PAX and PEP powders with average particle sizes of 40–60 μm were purchased from Agela Technologies (Tianjin, China). Certified reference materials for ATX-a, GYM, SPX1, AZA1, AZA2 and AZA3, OA, DTX1 and DTX2 were purchased from the Institute for Marine Bioscience of the National Research Council (NCR) (Halifax, Nova Scotia, Canada).

2.2. Samples collection and DMSPE procedure

The seawater samples were collected from three locations (Xiamen, Jinjiang, Dongshan) along the coastline of Fujian Province, China, with a sampling volume of 1.5 L in each location. Before pretreatment, each seawater sample was filtered through a 0.45 μm glass microfiber filter to remove some visible particles and algae. Then, 50 mL of seawater sample was accurately measured into a 50 mL Eppendorf tube with 15 mg PCX and 15 mg PAX adsorbents to perform the DMSPE procedure. After 30 s of vortex extraction, the analytes were adsorbed on the PCX and PAX adsorbents, and the extract was poured off into a 50 mL syringe with a 0.22 μm nylon microporous membrane. In this way, the extracting solution was removed, and the adsorbents enriched with the analytes were retained on the microporous membrane, which were eluted with 1.5 mL of ammonium hydroxide/MeCN (5:95 v/v) and 1.5 mL of formic acid/MeCN (5:95 v/v), respectively. The eluent was collected and evaporated to dryness under a gentle stream of nitrogen. Then, the residue was reconstituted with 500 μL of water/MeCN (1:1 v/v) and filtered by a 0.22 μm nylon filter for LC-HRMS analysis.

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