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水生动植物体内 PAEs 环境激素与食品中苏丹染料的 GC-EI-MS 分析方法研究

Study of Phthalic Acid Esters Environmental Incretion in Aquicolous propagation and of Sudan Dyes in Food by GC-EI-MS

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**Dissertation for Master of Analytical Chemistry**

**Study of Phthalic Acid Esters Environmental  
Incretion in Aquicolous biology and Sudan Dyes in  
Food by GC-EI-MS**

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## 摘 要

科技与社会的进步使得人们在接触和使用大量化学物质的同时,也在向环境排放大量的垃圾,造成了严重的生态环境问题,其中环境激素问题的研究进展尤其引人注目。邻苯二甲酸酯(Phthalic Acid Esters, PAEs)类环境激素作为增塑剂广泛存在于塑料制品中,随着塑料的大量生产和应用而释放到环境中,构成对生态的严重破坏和对人类的巨大威胁,有人将 PAEs 称为“第二个全球性 PCBs 污染物”。

本论文致力于水生动、植物体内 PAEs 含量的分析,建立了丙酮超声提取、Florisil 硅藻土净化预分离和 GC-EI-MS 定性与定量的分析方法,分析了多种水生动植物体内的 17 种 PAEs 类环境激素。内容分为四章:

第一章 简要地介绍了 PAEs 环境激素的国内外相关的研究情况。阐述了环境激素的概念、分类、污染与危害、研究进展,并综述了 PAEs 环境激素的简介及其分析方法,同时讨论了目前 PAEs 研究课题所存在的问题和研究前景,最后对该课题的研究内容进行了简单介绍,并对课题的后续研究进行了展望。

第二章 简述了 PAEs 气相色谱-电子轰击离子化质谱的选择离子监测(Gas Chromatography-Electron Impact Ionization Mass Spectrometry Selected Ions Monitoring, GC-EI-MS SIM)分析方法的建立。从 PAEs 的物理化学性质分析,探讨了不同气相色谱分析参数的设置,尤其是色谱柱程序升温的设置,确定采用恒温的方法使目标物达到基线分离。同时优化了质谱参数的设置,主要是质谱离子化方式的选择,决定采用 EI 方式。最后对 17 种 PAEs 化合物的 EI-MS 主要碎片离子的结构及其碎裂机理进行了初步解析,为 PAEs 类环境激素的定性与定量分析供依据,从而确定了 SIM 分析的特征碎片离子,建立了 PAEs 类环境激素 GC-EI-MS SIM 同时分析的分析方法。

第三章 开展了 GC-EI-MS 应用于水生动植物体内 17 种 PAEs 含量同时分析的方法研究。首先,优化了样品前处理过程中的提取剂种类、吸附剂种类及其去活化条件、洗脱剂种类及其配比、洗脱体积等实验条件;然后,讨论了分析空白值的质量控制,详细考察了各种可能导致实验室内污染的主要因素及其相应对策,同时进行了加标回收率实验,从方法检测限、准确度和精密度方面保证了分

析方法的可靠性；最后分析了多种水生动植物样品中 PAEs 的含量，证实 PAEs 类环境激素会在生物体内富集。

**关键词：**环境激素；邻苯二甲酸酯；PAEs；水生动植物；GC-EI-MS；分析空白。

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## ABSTRACT

With the development of science and technology, people touched and used lot of chemical materials, and emitted a mass of wastes at the same time, which made great harm to the environment especially the problem of Environmental Incretion. Phthalic Acid Esters which are a kind of Environmental Incretion consist extensively in the plastic materials as the additive. Along with the production and application of plastic products, PAEs were released in the environment and made bad effect to the zoology, which threatened the human beings. PAEs was called as “the second global PCBs pollutant” by someone.

This thesis was applied to analyze PAEs in organism. The method was as following, extracted in acetone, separated by Florisil diatomite, then analyzed by GC-EI-MS qualitatively and quantitatively. Seventeen PAEs were analyzed in aquicolous propagation. The whole thesis was divided in four parts.

The first part simply introduced the study of PAEs Environmental Incretion in China and abroad. The conception, research development, classed and pollution harmfulness of Environmental Incretion was explained. The character, application, toxicity, pollution status and analytical method of PAE was interpreted. Contemporarily, the problems and the meaning of the task was introduced. Then we made an expectation. At last, the content of the study was briefly shown.

The second part briefly introduced the establishment of the analytical method, Gas Chromatography-Electron Impact Ionization-Mass Spectrometry-Selected Ions Monitoring(GC-EI-MS SIM). The structures of PAEs fragments and their rupture mechanisms were parsed primarily to give mass messages detailedly in quantification. The parameters of GC instrument was set to discuss the effect made to the results. The temperature increasing process of the chromatography column was studied especially and constant temperature was used to separate the objects completely. The parameters of mass spectrometry was optimized to determine the use of ionization manner. Finally, characteristic fragments were chose to analyze by SIM mode.

The third part developed a GC-EI-MS method for simultaneous determination of seventeen PAEs in aquicolous propagation. Firstly, the extraction manner, selection of extractant, selection of sorbent, deactivation method of sorbent, styles of eluent,

proportion of eluent and the elution curve were optimized during the pretreatment process. Secondly, the control of analytical blank was studied to find the solution of pollution. Thirdly, the recoveries, limit of detection, accuracy, precision and linear range of the method were investigated in detail to pledge the quality. Finally, PAEs were analyzed in algae, fish, seashell, shellfish, cephalopod and dried samples.

The forth part developed a GC-EI-MS method for simultaneous determination of Sudan I and Sudan II in hot chili sauces and tomato sauces. Firstly, the structures of fragments and their rupture mechanisms were parsed primarily. Secondly, the pretreatment conditions, analytical parameters of instrument, qualitative and quantitative manner and injection manner were optimized. Finally, Linear Regression Equation, Correlation Coefficient, LOD, the recoveries and RSD of the method were investigated in detail to pledge the quality. Multiplicate hot chili sauces and tomato sauces were analyzed, and Sudan II was never detected while Sudan I was determined at any moment.

**Keyword:** Environmental Incretion, phthalic acid esters, PAEs, aquicolous propagation, Sudan I , Sudan II , GC-EI-MS.



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