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食品与电子电器产品中多溴联苯和多溴联苯醚残留的气相
色谱-质谱分析方法研究与应用

**Study and Application of Analytical Method for
Polybrominated Biphenyls and Polybrominated Diphenyl
Ethers Residue in Food and Electrical and Electronic
Products by Gas Chromatography-Mass Spectrometry**

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Polybrominated Biphenyls and Polybrominated Diphenyl
Ethers Residue in Food and Electrical and Electronic
Products by Gas Chromatography-Mass Spectrometry**

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摘 要

社会的进步使得人们越来越多地关注人类的健康,科学技术的发展也使得人们对食品安全性问题有了更多的了解。食品安全不仅影响消费者的健康,而且影响国际食品贸易的发展,甚至影响社会的稳定,因此食品安全问题已成为全世界普遍关心的热点问题。

本论文致力于食品和电子电器产品中多溴联苯(Polybrominated Biphenyls, PBBs)和多溴联苯醚(Polybrominated Diphenyl Ethers, PBDEs)残留的气相色谱-负离子化学源质谱联用(Gas Chromatography-Negative Chemical Ionization-Mass Spectrometry, GC-NCI/MS)分析方法研究与应用,开展了食品中 PBBs 和 PBDEs 残留 GC-NCI/MS 分析的超声提取法等样品前处理方法研究,优化了 GC/MS 的分析条件,初步建立了一些食品中 PBBs 和 PBDEs 残留的 GC-NCI/MS 分析方法。全部内容分为六章:

第1章 简要综述了食品中 PBBs 和 PBDEs 残留国内外相关的研究内容。阐述了 PBBs 和 PBDEs 污染、危害与研究进展,并综述了 PBBs 和 PBDEs 残留的分析方法研究进展,同时讨论了目前该研究课题存在的问题与研究前景,并对课题的后续研究进行了展望。

第2章 简述了 MS 谱图解析的基本原理。对 PBBs 和 PBDEs 的 NCI-MS 特征离子的断裂机理和分子结构进行了初步解析,为 PBBs 和 PBDEs 残留的 GC-NCI/MS 分析和检测提供分子结构信息。探讨了 10 种溴系阻燃剂 GC-NCI/MS 分析方法的建立,提出了 NCI-MS 应用于食品中 PBBs 和 PBDEs 残留分析的必要性及可行性。

第3章 初步建立了 GC-NCI-MS 同时分析深海鱼油食品中 5 种 PBDEs 残留的分析方法。深海鱼油食品用正己烷超声提取、中性和酸性硅胶层析柱净化和正己烷洗脱后,以 PCB-103 为内标物,采用 GC-NCI/MS 的选择离子监测方式(Selected Ion Monitoring, SIM)分析。当深海鱼油空白食品的加标质量浓度为 20 和 100 $\mu\text{g}/\text{kg}$ 时,加标回收率为 88.6%~111.3%,相对标准偏差为 3.8%~13.5%,方法检测限为 0.77~1.34 $\mu\text{g}/\text{kg}$,线性范围为 1~500 $\mu\text{g}/\text{kg}$,相关系数皆大于 0.9992,此方法成功

地应用于深海鱼油食品中 5 种痕量 PBDEs 残留的同时分析。

第4章 初步建立了 GC-NCI/MS 同时分析禽蛋食品中 5 种 PBBs 和 5 种 PBDEs 残留的分析方法。禽蛋食品用正己烷超声提取、中性和酸性硅胶层析柱净化和正己烷洗脱后,以 PCB-209 为内标物,采用 GC-NCI/MS 的 SIM 分析。当禽蛋空白食品的加标质量浓度为 5 和 50 $\mu\text{g}/\text{kg}$ 时,加标回收率为 75.2%~107%,相对标准偏差小于 8.76%,方法检测限为 0.14~0.39 $\mu\text{g}/\text{kg}$,线性范围为 1~250 $\mu\text{g}/\text{kg}$,相关系数皆大于 0.9991,此方法成功地应用于禽蛋食品中 10 种痕量 PBBs 和 PBDEs 残留的同时分析。

第5章 采用超声萃取-气相色谱电子捕获检测器法(Gas Chromatography-Electron Capture Detector, GC-ECD)初步建立了分析测定各种塑料制品中十溴二苯醚(BDE-209)的方法。塑料制品用正己烷等提取剂超声提取、中性和酸性硅胶层析柱净化和正己烷、二氯甲烷洗脱后,以 PCB-103 为内标物,采用 GC-ECD 分析。当塑料制品空白的加标质量浓度为 100、500 和 1000 $\mu\text{g}/\text{kg}$ 时,加标回收率为 92.1%~95.3%,相对标准偏差为 2.2%~8.9%,方法检测限为 8 $\mu\text{g}/\text{kg}$,线性范围为 50~10000 $\mu\text{g}/\text{kg}$,相关系数皆为 0.9994,此方法可完全满足电子电器产品中 PBDEs 和 PBBs 含量的分析检测工作的需要。

第6章 在开展以上论文研究的同时,还开展了福建省龙岩钙基膨润土进行钠化改型的研究,探索了钠化剂的选择及相关钠化条件对膨润土钠化效果的影响。选取了较佳的钠化剂为氟化钠;探讨了较佳的钠化条件,钠化温度 70 $^{\circ}\text{C}$,钠化剂用量 4.2%,矿浆浓度 10%,搅拌时间 90 min。在上述的研究条件下,经钠化改型后的钙基膨润土的膨胀容(V_B)为 33.5 mL/g,阳离子交换容量(Cation-exchange Capacity, CEC)为 114.0 m mol/100 g;经X射线衍射分析, $d(001)$ 值为 1.27145 nm,完全达到制备优良有机膨润土的质量要求。

关键词: 溴系阻燃剂;多溴联苯(PBBs);多溴联苯醚(PBDEs);鱼油;禽蛋;塑料;气相色谱-负离子化学源质谱(GC-NCI/MS);钙基膨润土;钠化剂;氟化钠;膨胀容;阳离子交换容量

ABSTRACT

People pay more attention to their own health because of the progress of the society, at the same time, people know more about the food security problem because of the development of science and technology. The food security not only affects the healthy of the consumer, but also affects progress of the international food trade, even affects the stabilization of the society. So the food security problem has been the hot problem all over the world. This dissertation focused on the analytical methods study and application on the polybrominated biphenyls (PBBs) and Polybrominated Diphenyl Ethers (PBDEs) residue in food.

This thesis focused on the studies of ultrasonic extraction technology used in the sample pretreatment and the optimization of the analytical conditions of gas chromatography mass spectrometry (GC-MS). The method for the multiresidue determination of PBBs and PBDEs in food had been established. The thesis consisted of six chapters.

The first chapter, simply introduced the study of PBBs and PBDEs 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 PBBs and PBDEs 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 chapter, briefly introduced the basic principle of the mass spectrum unscrambling, and in order to offer the structure information for the PBBs and PBDEs residue, analysed the negative chemical ionization mass spectrum (NCI-MS) unscrambling of 10 PBBs and PBDEs. This part briefly introduced the establishment of the analytical method, Gas Chromatography-Negative Chemical Ionization-Mass Spectrometry-Selected Ions Monitoring (GC-NCI-MS SIM). It was presented that the possibility and necessity of the application of gas chromatography negative chemical ionization mass spectrometry (GC-NCI-MS) to the analysis of PBBs and PBDEs residues in food.

The third chapter, an analytical multiresidue method for the simultaneous determination of 5 polybrominated diphenyl ethers (PBDEs) in fish oil was developed. PBDEs were extracted from fish oil with hexane and cleaned up on an acid silical gel column, then were determined by using a gas chromatography- mass spectrometry operated in negative chemical ionization mode and quantified in selective ion monitoring mode, and with PCB103 as internal standard. Meanwhile, fracture mechanism of some PBDEs negative chemical

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