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电喷雾萃取电离-串联质谱法测定不同水样中全氟辛酸

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摘要：全氟辛酸（PFOA）是一种持久性有机污染物，长期环境暴露会对生态系统与人类健康造成极大的风险，因此，发展快速定量监测水中 PFOA 的方法至关重要。本研究采用电喷雾萃取电离-串联质谱（EESI-MS/MS）法检测自来水、江水、河水中的痕量 PFOA。结果表明，在优化的实验条件下，PFOA 在 1～500 ng/L 浓度范围内的线性关系良好，线性相关系数（R^2）为 0.997 6，方法检出限（LOD）为 0.57 ng/L，定量限（LOQ）为 1.73 ng/L，回收率为 92.1%～105.2%，相对标准偏差（RSD，n=6）为 1.89%～5.45%。本方法具有灵敏度高、准确性好、分析速度快等优点，在监测环境水体污染物方面具有良好的应用前景。

关键词：电喷雾萃取电离-串联质谱（EESI-MS/MS）；快速检测；全氟辛酸（PFOA）；水

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Determination of Perfluorooctanoic Acids in Different Water Samples by Electrospray Extraction Ionization Tandem Mass Spectrometry

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Abstract: Water is a vital resource on the earth, serving as the foundation of life and playing a crucial role in our daily activities. Perfluorooctanoic acid (PFOA) is an organic compound, which poses a significant threat to the environment due to its persistence and bioaccumulation. PFOA exhibits various toxicities, including neurotoxicity, immunotoxicity, and carcinogenicity. It has been detected in worldwide of air and water samples, as it can easily move through different environmental media such as water, soil, and the atmosphere. The widespread distribution of PFOA in these media poses potential risks to both ecosystems and human health over the long term. Therefore, it is of utmost importance to develop a rapid detection method for accurately monitoring PFOA levels in water. In this study, the electrospray extraction ionization-tandem mass spectrometry (EESI-MS/MS) technique was utilized to directly and rapidly detect PFOA in tap water and river water. To achieve the highest

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ionization efficiency of PFOA in EESI-MS/MS across different water samples, the experimental parameters such as ion transfer tube temperature, spray voltage, electrospray solvent flow rate, and sample flow rate were optimized. The optimal conditions were temperature of 200 °C for the ion transfer tube, spray voltage of 2 kV, electrospray solvent flow rate of 4 μL/min, and sample flow rate of 6 μL/min. The experiments were conducted under negative ion mode with a mass scan range of *m*/*z* 50-500. Methanol solution was used as the electrospray solvent, and collision-induced dissociation (CID) was employed. The secondary characteristic fragment ion *m*/*z* 369 of *m*/*z* 413 for qualitative and quantitative analysis, enabling direct and rapid detection of PFOA in various water samples. The experimental results demonstrated good linearity of PFOA in the concentration range of 1-500 ng/L, with a linear correlation coefficient (R^2) of 0.9976. The detection limit (LOD) of the proposed method is 0.57 ng/L, and the limit of quantification (LOQ) is 1.73 ng/L. The recovery rate ranges from 92.1% to 105.2%, with a relative standard deviation (RSD, *n*=6) of 1.89%-5.45%. In summary, this method has the advantages of high sensitivity, accuracy, and fast analysis speed, without the need of sample pretreatment. The established EESI-MS/MS method can be effectively applied for direct and rapid detection of PFOA in different water samples, showing promising prospects for monitoring environmental water pollutants. Moreover, it provides valuable references and technical means for the detection of other pollutants.

Key words: electrospray extraction ionization-tandem mass spectrometry (EESI-MS/MS); rapid detection; perfluorooctanoic acid (PFOA); water

水是生命之源，普通成年人每天正常的饮水量约为 1 500～2 000 mL。环境中的化学物质能够通过饮用水进入人体，饮水暴露剂量主要取决于饮用水中污染物浓度、饮水量等因素，饮用水是否卫生、安全，直接影响人们的身体健康[1]。

全氟化合物（PFCs）是一类普遍存在的持久性和难降解的有机污染物，具有神经毒性、免疫毒性、生殖毒性和致癌性等，在天然水体中的含量范围约为几至几百 ng/L[2]，对人体健康造成严重威胁，已成为生活用水中新的潜在隐患。PFCs 存在于不同的环境介质中，对全球范围内的生物有毒害作用[3-6]。其中，全氟辛酸（PFOA）是生物群和人类生活过程中含量最丰富、最常见的一种 PFCs，具有分布广、毒性大、环境持久性和生物累积性等特征，能够对生态环境和人类健康造成严重和不可逆转的危害[7-10]。此外，PFOA 具有较强的化学稳定性、热稳定性及生物惰性等特点[11-13]，在环境中具有高度的移动性，广泛分布于水、土壤、大气等环境介质中[14-18]。人体暴露 PFOA 的途径主要是饮水摄入，其会对机体免疫器官、免疫功能以及免疫因子产生影响，进而导致相关的免疫疾病。因此，监测不同水样中 PFOA 含量意义重大。2019年，斯德哥尔摩公约批准增列 PFOA 等相关化合物为持久性有机污染物（POPs）受控物质；2020 年，欧盟 POPs 法规将 PFOA 列入管控范围；近年来，我国对 PFOA 实施严格管控，水质参考指标，即 PFOA 在生活饮用水的水质限值为 80 ng/L[19-20]。

目前，检测 PFOA 的方法主要有高效液相色谱-串联质谱（HPLC-MS/MS）法[21-27]、气相色谱-质谱（GC-MS）法[28-29]等。这些方法虽然具有高灵敏度、高准确度等优点，但存在费时费力、操作步骤繁琐等缺点，无法实现 PFOA 的直接快速检测。

基于此，本研究拟利用自制的电喷雾萃取电离源（EESI）结合 LTQ-XL 型线性离子阱质谱仪，快速检测不同水样中的 PFOA。希望为不同水样中 PFOA 的直接检测和快速监测提供技术手段，为环境水体中其他污染物的监管提供理论支持。

1　实验部分

1.1　主要仪器与装置

电喷雾萃取电离源：本实验室自制；LTQ-XL 型线性离子阱质谱仪：美国 Thermo Scientific 公司产品，配有 Xcalibur 数据处理系统；微量注射泵：英国保定兰格恒流泵有限公司产品；KQ3200DE

数控超声波清洗器：昆山市超声仪器有限公司产品；精密电子天平：瑞士 Mettler Toledo 公司产品。

EESI 源主要由相互独立的电喷雾通道和样品通道 2 部分构成[30]，示于图 1。EESI 源工作条件[31-32]：电喷雾通道及样品通道与质谱进样口之间角度 α=150°，距离 b=4 mm；电喷雾通道与样品通道之间角度 β=60°，间距 a=1.5 mm。

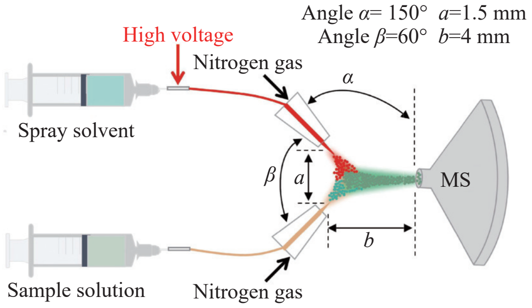


图 1　EESI 源装置示意图

Fig. 1　Schematic diagram of EESI

1.2　主要材料与试剂

全氟辛酸：北京曼哈格生物技术有限公司产品；甲醇（色谱纯）：德国默克公司产品；高纯氮气（99.999%）：南昌国滕气体有限公司产品；超纯水：北京费尔德科学仪器有限公司产品。

用甲醇配制 50 mg/L 全氟辛酸标准储备液和 1 mg/L 全氟辛酸标准使用液；萃取剂为甲醇；实际环境水样取自某市自来水、江水、河水。

1.3　质谱条件

负离子检测模式，质量扫描范围 m/z 50～500，电离电压 2.0 kV，离子传输管温度 200 ℃，毛细管电压−35 V，透镜电压−110 V，电喷雾溶剂流速 4 μL/min，样品流速 6 μL/min，雾化气（N_2，纯度 99.999%）压强 0.6 MPa。在进行 PFOA 标准溶液多级串联质谱检测时，母离子隔离宽 1.5 u，碰撞能量 6%，活化值 Q 为 0.25，碰撞时间 30 ms。其他检测参数由 LTQ-Tune 系统自动优化。

2　结果与讨论

2.1　PFOA 标准溶液的 EESI-MS/MS 分析

EESI-MS/MS 基于电喷雾通道喷出的甲醇溶液（即初级带电液滴）与样品通道喷出的样品液滴在三维空间中进行碰撞，进而实现了液-液萃取与电荷转移，并完成去溶剂化过程，供质谱检测[33-34]。采用 EESI-MS/MS 分析 PFOA 标准溶液，一级质谱图示于图 2a。进一步结合碰撞诱导解离（CID）实现对 PFOA 的定性检测，二级碎片离子信号 m/z 369、169[23, 35]为 PFOA 的质子化分子离子，示于图 2b。

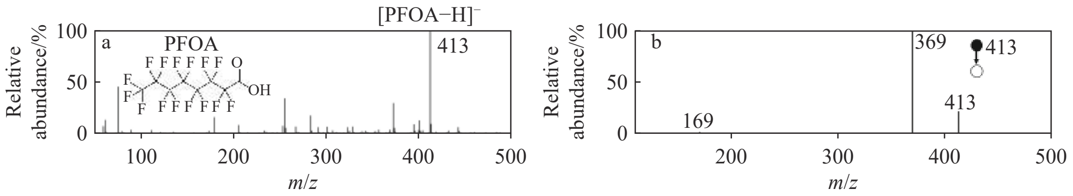


图 2　1 mg/L PFOA 的一级（a）和二级（b）质谱图

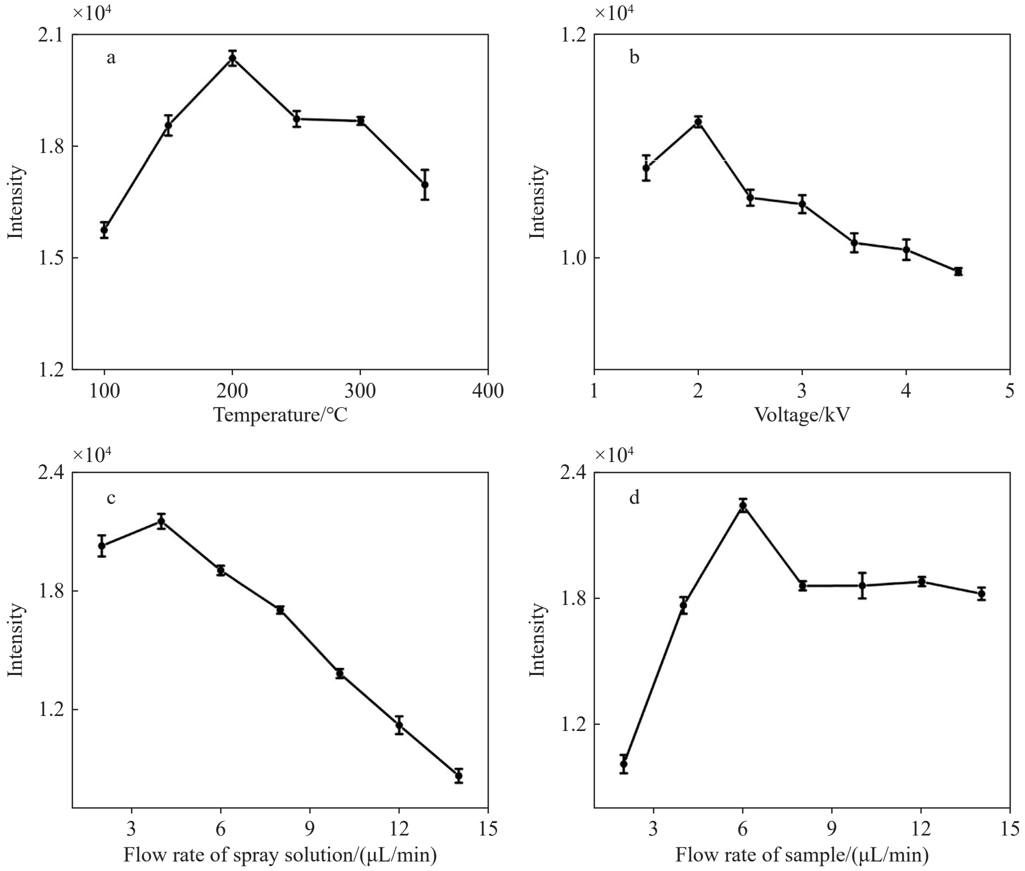
Fig. 2　MS (a) and MS^2 (b) spectra of 1 mg/L PFOA

2.2　EESI-MS/MS 参数的优化

为了使 EESI-MS/MS 对 PFOA 的离子化效率达到最佳，优化了离子传输管温度、喷雾电压、电喷雾溶剂流速、样品流速等参数。在负离子模式下，均选择 m/z 413 的二级特征碎片离子 m/z 369 的质谱响应强度来表示对 PFOA 的检测效率。

2.2.1　离子传输管温度　离子传输管温度会影响离子的去溶剂化效果，进而影响目标信号的强度，其优化结果示于图 3a。离子传输管温度在 100～400 ℃ 范围内，目标离子的质谱响应强度呈先升高后降低的趋势，接近 200 ℃ 时，响应强度最大。因此，选择离子传输管温度为 200 ℃。

2.2.2　喷雾电压　本实验考察了喷雾电压在 1.5～4.5 kV 范围内对质谱响应强度的影响，结果示于图 3b。当喷雾电压大于 2.0 kV 时，质谱响应强度呈下降趋势，推测原因为喷雾电压过高导致喷雾口发生电晕放电，降低了离子的形成效率，使目标信号强度降低。因此，选择喷雾电压为 2.0 kV。



注：a. 离子传输管温度；b. 喷雾电压；c. 电喷雾溶剂流速；d. 样品流速

图 3　不同实验条件对 PFOA 信号强度的影响

Fig. 3　Effects of different experiment conditions on PFOA signal intensity

2.2.3　电喷雾溶剂流速　本实验考察了电喷雾溶剂流速在 2～14 μL/min 范围内对质谱响应强度的影响，结果示于图 3c。当流速大于 4 μL/min 时，信号强度降低，表明流速过高会导致离子化效率降低。因此，选择电喷雾溶剂流速为 4 μL/min。

2.2.4　样品流速　本实验考察了样品流速在 2～14 μL/min 范围内对质谱响应强度的影响，结果示于图 3d。可见，目标物信号强度呈先升高后降低的趋势，当样品流速大于 6 μL/min 时，信号强度降低。推测原因为样品流速过大会减弱样品的雾化效率，进而降低目标离子的质谱响应强度。因此，选择样品流速为 6 μL/min。

2.3　PFOA 的定量分析

2.3.1　线性关系、检出限与定量限　配制 1、10、50、100、250、500 ng/L PFOA 水溶液，在优化的实验条件下进行直接质谱分析，并选择 m/z 413 的二级特征碎片离子 m/z 369 作为定量离子进行分析。以 PFOA 水溶液的质量浓度为横坐标，以目标离子的 5 次平均质谱信号强度为纵坐标绘制标准曲线，线性回归方程为 $y=10.366\,0x+173.617\,2$，示于图 4。PFOA 在 1～500 ng/L 浓度范围内呈现良好的线性关系，线性相关系数（R^2）为 0.997 6。当信噪比（S/N）=3.3 时，根据 LOD=$3.3\sigma/b$[36]（σ 为空白标准偏差，b 为斜率）计算检出

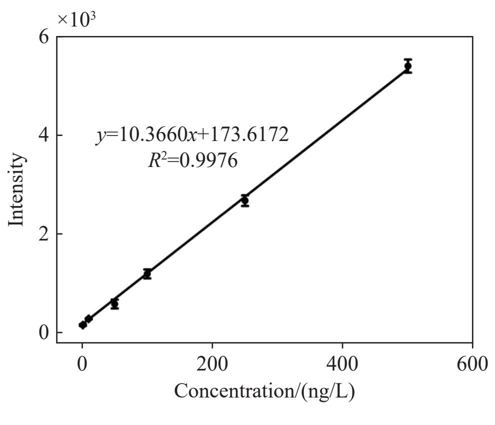


图 4　PFOA 的校准曲线

Fig. 4　Calibration curve of PFOA

限为 0.57 ng/L；当 $S/N=10$ 时，根据 $\mathrm{LQD}=10\sigma/b$[36] 计算定量限为 1.73 ng/L。

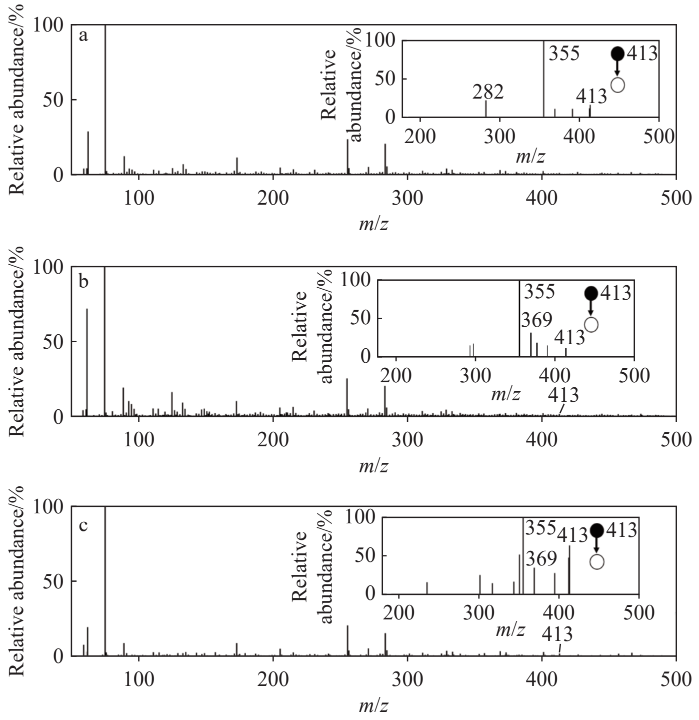
2.3.2　精密度和准确度　选择不同水样作为基质评价方法的精密度和准确度，分别配制 3、30、300 ng/L 加标溶液，在优化的实验条件下，采用 EESI-MS/MS 测定不同水样中的 PFOA，重复测定 6 次，结果列于表 1。PFOA 在自来水中的回收率为 92.1%～104.9%，相对标准偏差（RSD）为 1.89%～4.49%；在江水中的回收率为 99.2%～105.2%，RSD 为 2.99%～5.45%；在河水中的回收率为 92.3%～102.6%，RSD 为 2.82%～3.68%。

2.3.3　实际样品分析　采用 EESI-MS/MS 技术直接检测自来水、江水、河水中的 PFOA，以 m/z 413 为母离子，通过碰撞诱导解离（CID）进行检测，结果示于图 5。结果表明，自来水中未检出 PFOA；江水、河水中 PFOA 的残留水平分别低于 30、52 ng/L。此外，将本研究方法与高效液相色谱-串联质谱（HPLC-MS/MS）法进行对比，结果列于表 2。可见，本方法可用于直接快速检测不同水样中痕量 PFOA。

表 1　加标样品的分析结果（n=6）

Table 1　Analytical results of spiked samples (n=6)

样本 Sample	样本本底值 Sample background value/(ng/L)	加标量 Added value/(ng/L)	测量值 Measured value/(ng/L)	回收率 Recovery rate/%	相对标准偏差 RSD/%
自来水	ND	3	2.76	92.1	4.49
		30	27.96	93.2	4.45
		300	314.82	104.9	1.89
江水	29.86	3	32.83	99.2	3.67
		30	61.43	105.2	5.45
		300	341.02	103.7	2.99
河水	51.78	3	54.55	92.3	3.68
		30	81.93	100.5	2.97
		300	359.51	102.6	2.82



注：a. 自来水；b. 江水；c. 河水

图 5　实际样品的质谱图

Fig. 5　Mass spectra of actual samples

表 2　EESI-MS/MS 和 HPLC-MS/MS 对环境水体的分析结果

Table 2　Analysis results of environmental water by EESI-MS/MS and HPLC-MS/MS

方法 Method	样品 Sample	PFOA含量 Content of PFOA/(ng/L)	线性范围 Linear range/(ng/L)	检出限 LOD/(ng/L)	单个样品分析时间 Analysis time of single sample/min
EESI-MS/MS	自来水	ND	1～500	0.57	1
	江水	29.86			
	河水	51.78			
HPLC-MS/MS	自来水	ND	50～1000^{a}	10^{a}	5^{a}
	江水	29.42			
	河水	54.19			

注: a表示数据引用自参考文献[37]

3　结论

本研究采用 EESI-MS/MS 技术快速定性、定量分析不同水样中的 PFOA, 并优化了离子传输管温度、喷雾电压、电喷雾溶剂流速、样品流速等实验条件。结果表明, 本方法可快速灵敏、高效准确地检测不同水样中的 PFOA, 在监测环境水体污染物方面具有良好的应用前景, 适用于不同环境中 PFOA 的直接快速检测。

参考文献:

[1] 黄建洪, 张琴, 王晋昆, 崔祥芬. 水环境污染健康风险评价中饮水量暴露参数的研究进展[J]. 卫生研究, 2021, 50(1): 146-153.

HUANG Jianhong, ZHANG Qin, WANG Jinkun, CUI Xiangfen. Research progress on exposure parameters of drinking water quantity in health risk assessment of water environmental pollution[J]. Journal of Hygiene Research, 2021, 50(1): 146-153(in Chinese).

[2] STAHL T, MATTERN D, BRUNN H. Toxicology of perfluorinated compounds[J]. Environmental Sciences Europe, 2011, 23(1): 38.

[3] NIU J, LI Y, SHANG E, XU Z, LIU J. Electrochemical oxidation of perfluorinated compounds in water[J]. Chemosphere, 2016, 146: 526-538.

[4] ALBERT K, HSIEH P Y, CHEN T H, HOU C H, HSU H Y. Diatom-assisted biomicroreactor targeting the complete removal of perfluorinated compounds[J]. Journal of Hazardous Materials, 2020, 384: 121 491.

[5] TIAN H, GU C. Effects of different factors on photodefluorination of perfluorinated compounds by hydrated electrons in organo-montmorillonite system[J]. Chemosphere, 2018, 191: 280-287.

[6] YEA Y, KIM G, WANG D, KIM S, YOON Y, ELANCHEZHIYAN S S, PARK C M. Selective sequestration of perfluorinated compounds using polyaniline decorated activated biochar[J]. Chemical Engineering Journal, 2022, 430: 132 837.

[7] KHAN M Y, SONG J, NARIMANI M, Da SILVA G. Thermal decomposition mechanism and kinetics of perfluorooctanoic acid (PFOA) and other perfluorinated carboxylic acids: a theoretical study[J]. Environmental Science: Processes & Impacts, 2022, 24(12): 2 475-2 487.

[8] LIU Y, BAO J, HU X M, LU G L, YU W J, MENG Z H. Optimization of extraction methods for the analysis of PFOA and PFOS in the salty matrices during the wastewater treatment[J]. Microchemical Journal, 2020, 155: 104 673.

[9] LIANG L, PAN Y, BIN L, LIU Y, HUANG W, LI R, LAI K P. Immunotoxicity mechanisms of perfluorinated compounds PFOA and PFOS[J]. Chemosphere, 2022, 291(Pt 2): 132 892.

[10] GANBAT N, ALTAEE A, ZHOU J L, LOCKWOOD T, AL-JUBOORI R A, HAMDI F M, KARBASSIYAZDI E, SAMAL A K, HAWARI A, KHABBAZ H. Investigation of the effect of surfactant on the electrokinetic treatment of PFOA contaminated soil[J]. Environmental Technology and Innovation, 2022, 28: 102 938.

[11] PONTIUS. Regulation of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) in drinking water: a comprehensive review[J]. Water, 2019, 11(10): 2 003.

[12] MAO T, SHI X, LIN L, CHENG Y, LUO X, FANG C. Research progress on up-conversion fluorescence probe for detection of perfluorooctanoic acid in water treatment[J]. Polymers, 2023, 15(3): 605.

[13] LUNDQUIST N A, SWEETMAN M J, SCROGGIE K R, WORTHINGTON M J H, ESDAILE L J, ALBOAIJI S F K, PLUSH S E, HAYBALL J D, CHALKER J M. Polymer supported carbon for safe and effective remedia-

tion of PFOA- and PFOS-contaminated water[J]. ACS Sustainable Chemistry & Engineering, 2019, 7(13): 11 044-11 049.

[14] JIAN J M, GUO Y, ZENG L, LIU L Y, LU X, WANG F, ZENG E Y. Global distribution of perfluorochemicals (PFCs) in potential human exposure source-a review[J]. Environment International, 2017, 108: 51-62.

[15] SUWANNAKOT P, LISI F, AHMED E, LIANG K, BABARAO R, GOODING J J, DONALD W A. Metal-organic framework-enhanced solid-phase microextraction mass spectrometry for the direct and rapid detection of perfluorooctanoic acid in environmental water samples[J]. Analytical Chemistry, 2020, 92(10): 6 900-6 908.

[16] BARTELL S M. Online serum PFOA calculator for adults[J]. Environmental Health Perspectives, 2017, 125(10): 104 502.

[17] PAN Y, SHI Y, WANG J, CAI Y. Evaluation of perfluorinated compounds in seven wastewater treatment plants in Beijing urban areas[J]. Science China Chemistry, 2011, 54(3): 552-558.

[18] 王懿, 孔德洋, 单正军, 谭丽超. 加速溶剂萃取-固相萃取净化-超高效液相色谱串联质谱法测定土壤中 11 种全氟化合物[J]. 环境化学, 2012, 31(1): 113-119.

WANG Yi, KONG Deyang, SHAN Zhengjun, TAN Lichao. Analysis of perfluorinated compounds in soil by accelerated solvent extraction combined with ultra performance liquid chromatographytandem mass spectrometry[J]. Environmental Chemistry, 2012, 31(1): 113-119 (in Chinese).

[19] 涂伟文. 纺织品防水防油剂的历史、现状和发展方向[J]. 印染, 2022, 48(5): 82-89, 93.

TU Weiwen. History, current situation and future of water-and oil-repellents for textiles[J]. China Dyeing & Finishing, 2022, 48(5): 82-89, 93(in Chinese).

[20] GB 5749—2022 生活饮用水卫生标准[S]. 北京: 中国标准出版社, 2022.

[21] GROFFEN T, BERVOETS L, JEONG Y, WILLEMS T, EENS M, PRINSEN E. A rapid method for the detection and quantification of legacy and emerging per- and polyfluoroalkyl substances (PFAS) in bird feathers using UPLC-MS/MS[J]. Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences, 2021, 1 172: 122 653.

[22] 郭斐斐, 王雨昕, 李敬光, 张加玲, 赵云峰, 吴永宁. 超高效液相色谱-串联质谱法测定人尿液中全氟有机化合物[J]. 色谱, 2011, 29(2): 126-130.

GUO Feifei, WANG Yuxin, LI Jingguang, ZHANG Jialing, ZHAO Yunfeng, WU Yongning. Determination of perfluorinated compounds in human urine by ultra high performance liquid chromatographytandem mass spectrometry[J]. Chinese Journal of Chromatography, 2011, 29(2): 126-130(in Chinese).

[23] 杨文龙, 郭靖, 杜伟, 吴华, 吕美玲, 董亮, 杜兵, 黄业茹. 超高效液相色谱-新型串联四极杆质谱法测定环境水体与土壤中的全氟辛酸和全氟辛烷磺酸[J]. 环境化学, 2018, 37(12): 2 820-2 823.

YANG Wenlong, GUO Jing, DU Wei, WU Hua, LYU Meilin, DONG Liang, DU Bing, HUANG Yeru. Determination of perfluorooctanoic acid and perfluorooctanesulfonates in environmental water and soil matrixes using ultra high performance liquid chromatography coupled with state-of-art tandem quadrupole mass spectrometry[J]. Environmental Chemistry, 2018, 37(12): 2 820-2 823(in Chinese).

[24] ABDELRAHEEM E, WISE J, MURPHY C, JIANG W. Triple-stage quadrupole mass spectrometer to determine ubiquitously present per- and polyfluorinated alkyl substances in drinking water at part per trillion levels using solid phase extraction approach[J]. Bulletin of Environmental Contamination and Toxicology, 2022, 110(1): 32.

[25] LIU L, YAN P, LV J, LIU X, ZHAO J, GUO J, LIU G, BIAN X, GAO L, YAN W, HUANG Q, CHEN G. Optimization and application of a method to determine 24 perfluorinated compounds in umbilical cord serum by using liquid chromatography tandem mass spectrometry[J]. Journal of Chromatography B, Analytical Technologies in the Biomedical and Life Sciences, 2022, 1 207: 123 365.

[26] 王浩, 邵明媛, 贾婧怡, 刘明艳, 裴帆. 液相色谱-串联质谱法同时测定婴幼儿配方乳粉中全氟辛酸、全氟辛烷磺酸、双酚 A 和壬基酚残留[J]. 色谱, 2018, 36(12): 1 279-1 283.

WANG Hao, SHAO Mingyuan, JIA Jingyi, LIU Mingyan, PEI Fan. Simultaneous determination of perfluoric acid, perfluorooctane sulfonic acid, bisphenol A, nonylphenol in infant milk powder by high-performance liquid chromatography-tandem mass spectrometry[J]. Chinese Journal of Chromatography, 2018, 36(12): 1 279-1 283(in Chinese).

[27] WU M, SUN R, WANG M, LIANG H, MA S, HAN T, XIA X, MA J, TANG L, SUN Y, XU G. Analysis of perfluorinated compounds in human serum from the general population in Shanghai by liquid chromatography-tandem mass spectrometry (LC-MS/MS)[J]. Chemosphere,

2017, 168: 100-105.

[28] SCOTT B F, MOODY C A, SPENCER C, SMALL J M, MUIR D C G, MABURY S A. Analysis for perfluorocarboxylic acids/anions in surface waters and precipitation using GC-MS and analysis of PFOA from large-volume samples[J]. Environmental Science & Technology, 2006, 40(20): 6 405-6 410.

[29] SHAFIQUE U, SCHULZE S, SLAWIK C, KUNZ S, PASCHKE A, SCHÜÜRMANN G. Gas chromatographic determination of perfluorocarboxylic acids in aqueous samples-a tutorial review[J]. Analytica Chimica Acta, 2017, 949: 8-22.

[30] 董晓峰, 刘林, 王姜, 许柠, 顾海巍, 周书民, 陈焕文. 电喷雾萃取电离源调节装置的研制[J]. 质谱学报, 2014, 35(3): 226-231.
DONG Xiaofeng, LIU Lin, WANG Jiang, XU Ning, GU Haiwei, ZHOU Shumin, CHEN Huanwen. Development of adjustable device for extractive electrospray ionization with improved performance[J]. Journal of Chinese Mass Spectrometry Society, 2014, 35(3): 226-231(in Chinese).

[31] 许柠, 朱志强, 杨水平, 王姜, 顾海巍, 周振, 陈焕文. 新型电喷雾萃取电离质谱法快速标靶分析氨基酸[J]. 分析化学, 2013, 41(4): 523-528.
XU Ning, ZHU Zhiqiang, YANG Shuiping, WANG Jiang, GU Haiwei, ZHOU Zhen, CHEN Huanwen. Direct detection of amino acids using extractive electrospray ionization tandem mass spectrometry[J]. Chinese Journal of Analytical Chemistry, 2013, 41(4): 523-528(in Chinese).

[32] 贾滨, 张兴磊, 丁健桦, 杨水平, 陈焕文. 电喷雾萃取电离质谱技术及其应用进展[J]. 科学通报, 2012, 57(20): 1 918-1 927.
JIA Bin, ZHANG Xinglei, DING Jianhua, YANG Shuiping, CHEN Huanwen. Principle and applications of extractive electrospray ionization mass spectrometry[J]. Chinese Science Bulletin, 2012, 57(20): 1 918-1 927(in Chinese).

[33] ZHU L, HU Z, GAMEZ G, LAW W S, CHEN H, YANG S, CHINGIN K, BALABIN R M, WANG R, ZHANG T, ZENOBI R. Simultaneous sampling of volatile and nonvolatile analytes in beer for fast fingerprinting by extractive electrospray ionization mass spectrometry[J]. Analytical and Bioanalytical Chemistry, 2010, 398(1): 405-413.

[34] CHEN H W, HU B, ZHANG X. Principle and application of ambient mass spectrometry for direct analysis of complex samples [J]. Chinese J Anal Chem, 2010, 38(8): 1 069-1 088.

[35] TAHZIZ A, MOHAMAD HARON D E, AZIZ M Y. Liquid chromatographic tandem mass spectrometric (LC-MS/MS) determination of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the yolk of poultry eggs in Malaysia[J]. Molecules, 2020, 25(10): 2 335.

[36] SHRIVASTAVA A, GUPTA V. Methods for the determination of limit of detection and limit of quantitation of the analytical methods[J]. Chronicles of Young Scientists, 2011, 2(1): 21.

[37] 朱晓玲, 赵颖, 白立雯. 超高效液相色谱-质谱法测定地下水中全氟辛酸 (PFOA) 和全氟辛基磺酸 (PFOS)[J]. 化学研究与应用, 2022, 34(12): 3 004-3 008.
ZHU Xiaoling, ZHAO Ying, BAI Liwen. Analysis of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) substances in groundwater with ultra-high performance liquid chromatography-tandem mass spectrometry[J]. Chemical Research and Application, 2022, 34(12): 3 004-3 008(in Chinese).

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