新污染物分析应用文集

SCIEX
The Power of Precision

SCIEX 质谱 -- 超过 50 年的创新历程

SCIEX 在质谱技术领域拥有超过 50 年的创新经验。从 1981 年致力于开发突破性的技术和解决方案。

SCIEX 创立

由 Barry French 博士和 William Breukelman博士共同创立于**多伦多大学**

1970

1981

发布**第一款SCIEX的商用三重四极杆**(MS/MS)仪器

1989

发布API III，是**第一款SCIEX的商业化的液质联用系统**

2001

发布API 4000™ LC-MS/MS 系统，成为了**生物分析**的标准手段

2002

发布QTRAP® LC-MS/MS 系统，**SCIEX创新的把三重四极杆和线性离子阱技术结合起来**

2005

发布API 5000™系统，该系统是代表**当时先进水平的三重四极杆液质联用系统**

2008

发布5500系列，这是**业界知名的液相色谱三重四极杆质谱系统**

2009

成为**丹纳赫集团**的一员，并于2010年**收购Eksigent公司液相业务**

2012

SCIEX在这一年发布新产品数量创新高，这其中包括**SWATH®采集技术**

2013

整合了**Beckman Coulter®**公司毛细管电泳业务

SCIEX
The Power of Precision

成功推出第一台 SCIEX 的商业化三重四极杆质谱系统开始，一直

发布第一款SCIEX的用于台式精确质量质谱系统，**X500R QTOF 系统**
发布**SCIEX Now™**客户服务平台

2015

五十周年纪念

2018

2020

发布**Echo™ MS系统**，这是一款基于**声波激发耦合质谱(AEMS)**技术的超高检测样品通量的系统

发布专门控制三重四极杆质谱的**SCIEX OS 软件**，是SCIEX创新的核心动力

发布**SCIEX Triple Quad™ 7500 系统**，开启灵敏度的新时代

发布**C100HT 生物制品分析系统**，**OptiFlow™ Turbo V 离子源**，和**StatusScope® 远程监控**服务

2021

发布**ZenoTOF™ 7600系统**，这是一款高分辨精确质量质谱，是SCIEX跨跃式的质谱创新发展

发布**BioPhase™ 8800 系统**，一款可以同时检测8份样品的多通道毛细管电泳系统

发布了**SCIEX OS软件3.0版本**，支持中文界面

2022

发布**ExionLC™ 2.0和ExionLC™ 2.0+ 系统**，与SCIEX质谱系统兼容，实现一体化控制

期待未来

发布**Zeno™ SWATH® 数据非依赖性采集(Zeno™ SWATH DIA®)**技术，标志着生物标志物发现及转化应用中又向前迈进了重要一步

质谱赋能丨SCIEX 质谱助力新污染物治理新篇章

2022 年 5 月，国务院办公厅印发的《新污染物治理行动方案》指出，到 2025 年，建立健全化学物质环境风险管理法规制度体系和有毒有害化学物质环境风险管理体制，动态发布《重点管控新污染物清单》；完成国内外高关注、高产（用）量的化学物质危害筛查，完成一批化学物质环境风险评估，新污染物治理能力明显增强。

新污染物（Emerging Contaminants，简称 ECs）不同于常规污染物，指新近发现或被关注，对生态环境或人体健康存在风险，尚未纳入管理或者现有管理措施不足以有效防控其风险的污染物。现阶段国际上主要关注的新污染物包括：环境内分泌干扰物、全氟化合物等持久性有机污染物、抗生素、微塑料等四大类。

新污染物具有生物毒性、环境持久性和生物累积性等特征，在环境中即使浓度较低，也可能具有显著的环境与健康风险，其危害具有潜在性和隐蔽性。由于环境样品基质复杂，新污染物监测面临的挑战有：在环境中含量较低且基质复杂，同时样品数量大。液质技术已成为越来越多研究者和检测平台都采用的高灵敏度、高通量的新污染物筛查和监测不可或缺的分析方法。

SCIEX 一直是质谱前沿技术的引领者，针对新污染调查和监测具有完备的新污染物监测解决方案，依托高灵敏、抗基质干扰的液质联用仪，完全满足痕量级别的新污染物监测工作要求，具备高灵敏度、高稳定性和高覆盖率的技术优势。

内容提要

直接进样法测定饮用水中全氟化合物的解决方案

A Solution for the Determination of Perfluorinated Compounds(PFCs) in Drinking Water by Direct Injection with SCIEX Triple Quad™ 3500 Systerm

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Key Words: LC-MS/MS, Perfluorinated Compounds (PFCs), Drinking Water, Triple Quad™ 3500

饮用水的安全问题一直以来是备受大家关注的问题，我们平时常关注的影响水质安全的指标主要有微生物、重金属、消毒副产物和其它有毒性的有机和无机物质的含量。近年来，有一种物质悄然的成为饮用水安全的潜在隐患-全氟化合物。

全氟化合物（PFCs）是一种人工合成的化学物质，它是一类具有特殊结构的有机化合物（碳相连的氢元素全都被氟元素所取代）。PFCs结构的特殊性赋予了其很强的化学稳定性，从而使PFCs在工业产品和家用产品制造领域得到广泛应用。随着其应用越来越广，其排放量也在不断增加，最终PFCs会回到环境和水体中。由于其化学稳定性强，所以很难被氧化和降解，如果水体中的PFCs浓度较高进入人体中会对人体带来伤害，所以需要对其浓度进行准确检测和严格把控。

本文选取了11种典型的全氟化合物，采用直接进样的方式，在SCIEX Triple Quad™ 3500 LC-MS/MS系统上，建立了饮用水中全氟化合物的快速测定方法，为饮用水中全氟化合物的监测提供了快速有效的技术支持。

本方法具有以下特点：

1. 本方法灵敏度高，11种化合物的检测灵敏度均达到ng/L级别
2. 本方法分析时间仅为7分钟，大大提高了通量
3. 本方法提供了11种全氟化合物的质谱条件、液相条件，拿来即用
4. 本方法采用大体积直接进样的方法，省去繁琐的样品前处理过程

仪器设备

SCIEX ExionLC™系统+ SCIEX Triple Quad™ 3500系统

RUO-MKT-02-13694-ZH-A

内容提要

样品前处理

- 饮用水过滤后，进行LC-MS/MS分析

液相方法

色谱柱：Phenomenex Kinetex F5
（100 × 3.0 mm, 2.6 µm ）

流动相：A：水（0.01%甲酸）；

B：乙腈

流速：0.5 mL/min；

柱温：40℃

梯度洗脱

时间（min）	A (%)	B (%)
0.00	97	30
2.50	97	65
4.00	85	99
5.00	25	99
5.10	5	30
7.00	97	30

质谱方法

离子源：ESI源，负离子模式

离子源参数：

IS电压: -4500 V　　气帘气 CUR: 25 psi

雾化气 GS1: 50 psi　　辅助气 GS2: 60 psi

源温度 TEM: 550℃　　碰撞气 CAD: 8 psi

备注：各化合物质谱参数见附表

实验结果

1. 11种化合物的典型色谱图

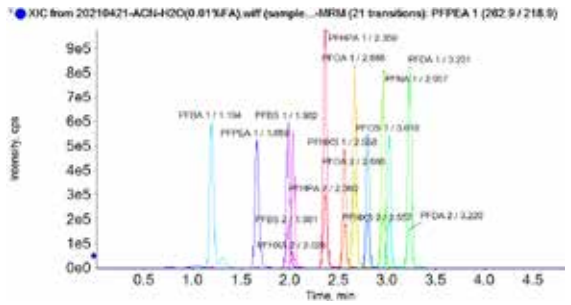

图1. 自来水中11种全氟化合物的色谱图

2. 11种化合物的检测灵敏度达ng/L级别，满足实际样品的测定需求

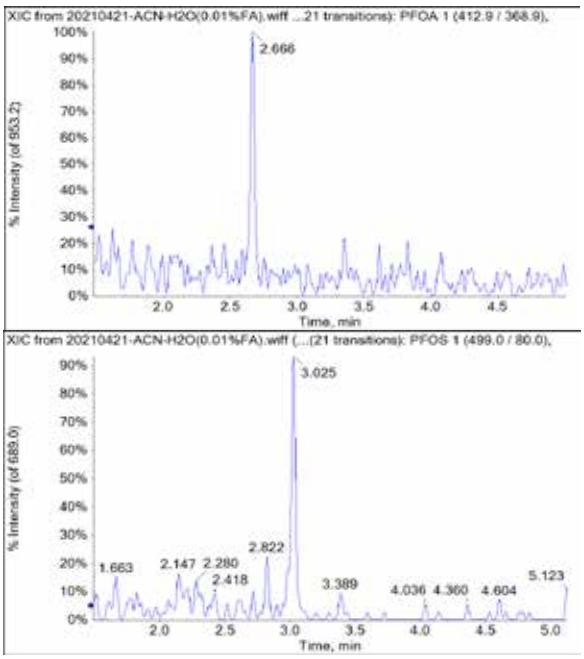

图2. 自来水中1ng/L PFOA和PFOS色谱图

3. 该方法的基质效应考察：11种化合物在三个浓度水平下的基质效应在80%-113%之间。

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内容提要

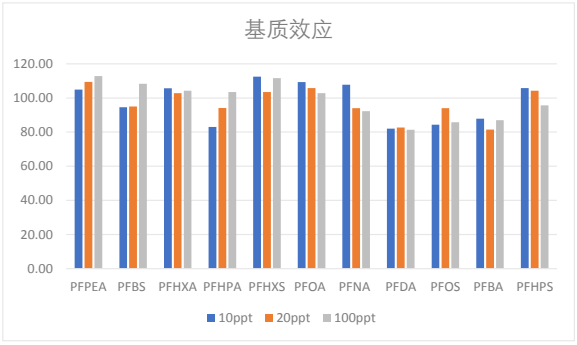

图3. 自来水中各化合物基质效应统计图

4. 该方法的线性关系好，r >0.99，且该方法重现性好，连续进样1000针后CV% < 2%。

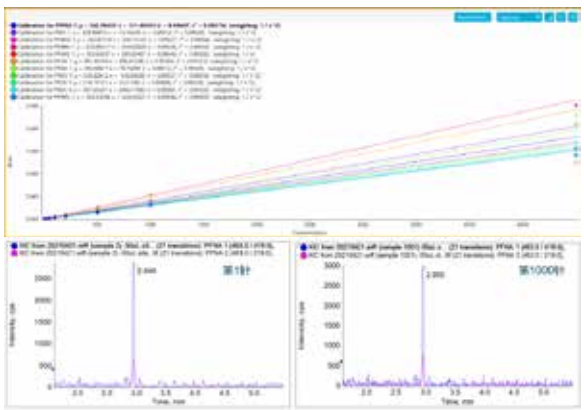

图4. 自来水中各化合物线性及重现性图谱展示

总结

本方法在SCIEX Triple Quad™ 3500 系统上建立了一套快速测定饮用水中11种典型全氟化合物的LC-MS/MS方法。该方法分析时间短，灵敏度高，满足饮用水中痕量PFCs残留的测定。该方法采用大体积直接进样的方式，无需SPE富集，简单易操作。

附表： 11种全氟化合物的质谱参数

Compound	Q1	Q3	DP	CE
全氟丁酸PFBA	212.9	168.9	-5	-12
全氟戊酸 PFPEA	262.9	218.9	-40	-11
	262.9	69	-40	-55
全氟丁烷磺酸钾 (全氟丁基磺酸) PFBS	298.9	80	-70	-65
	298.9	99	-70	-36
全氟己酸 PFHXA	312.9	268.9	-50	-11
	312.9	119	-50	-26
全氟庚酸 PFHPA	362.9	318.9	-30	-13
	362.9	168.9	-30	-21
全氟己基磺酸 PFHXS	398.9	80	-70	-75
	398.9	99	-70	-79
全氟辛酸 PFOA	412.9	368.9	-30	-15
	412.9	168.9	-34	-25
全氟庚烷磺酸 PFHPS	448.7	79.9	-100	-104
	448.7	98.9	-100	-88
全氟壬酸 PFNA	463	419	-50	-15
	463	219	-50	-22
十七氟辛烷磺酸 (全氟辛烷磺酸) PFOS	499	80	-90	-108
	499	99	-90	-97
十九氟癸酸 (全氟癸酸) PFDA	512.9	468.9	-31	-16
	512.9	218.9	-33	-24

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内容提要

饮用水中56种全氟及多氟化合物的LC-MS/MS解决方案

Analysis of 56 Perfluorinated and Polyfluorinated Compounds in Drinking Water by LC-MS/MS

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Key Words: Perfluorinated and Polyfluorinated Compounds, Drinking Water , LC-MS/MS

自2009年以来，传统全氟烷基化合物如全氟辛烷羧酸及其盐类（PFOA）和全氟辛烷磺酸及其盐类（PFOS）已被纳入国际《斯德哥尔摩公约》持久性污染物名单，用于限制该类化合物在全球范围内的生产和使用。鉴于其在生产中的不可或缺性，随着各种限制法规的出台，各大氟化工生产商开始加大新型含氟替代品研发力度，如采用结构类似全氟烷基醚类取代它们。这类化合物的半衰期比PFOA短，但是其毒性与PFOA类似且往往没有监管，且在地表水和饮用水中已有检出[1-2]。因此，建立水中同时检测全氟和多氟化合物（PFASs）的方法，对于环境中PFASs的长期监测和研究工作具有重要意义。本文利用SCIEX ExionLC™ 系统和SCIEX Triple Quad™系统建立了饮用水中56种PFASs的LC-MS/MS解决方案。

本实验方法具有如下特点：

- **化合物涵盖范围广**：包括全氟羧酸、全氟磺酸、全氟辛基磺酰胺、全氟磺酰胺基乙酸、调聚物磺酸盐、氟调醇、多氟膦酸及其它全氟替代物，8类56种；
- **高通量**：一针进样只需要12分钟，可同时测定56种PFASs并准确定量；
- **前处理方法简单**：样本只需要简单的稀释之后就直接进样；
- **灵敏度高**：56种PFASs均可达到pg级检测需求；

1.实验部分

1.1样品前处理

由于PFASs的广泛存在，样品容器可使用聚乙烯和聚丙烯材料做成的容器如试管，烧怀等。水样以8000 r/min转速离心5 min后，取出0.7 mL加入0.3 mL甲醇涡旋混匀，供LC-MS/MS进样分析。

1.2 色谱条件

色谱柱：Phenomenex Kinetex，F5 (2.6 µm, 3.0 × 100 mm)

流动相：A相：水（含2 mM甲酸铵）

B相：甲醇

流速：0.4 mL/min

洗脱程序：梯度洗脱（表1）

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内容提要

表1. 液相洗脱程序

时间（min）	A 相(%)	B 相(%)
0.0	80	20
2.0	40	60
6.0	5	95
10.0	5	95
10.1	80	20
12.0	80	20

1.3 质谱条件

离子源：电喷雾电离（electrospray ionization, ESI），负离子模式

离子源参数

气帘气CUR: 30 psi；　　源温度TEM: 350℃；

碰撞气CAD: 中；　　喷雾气GS1: 50 psi；

辅助加热气GS2: 55 psi；　　IS电压:-3500V；

离子对信息（表2）

2.结果与讨论

2.1 色谱条件优化

在本实验中化合物种类及数量较多，为了保证每个化合物都有较好的色谱保留及峰形，对色谱柱和流动相进行了优化。

对比了不同厂家及不同填料的色谱柱，其中Phenomenex F5 能够提供更好的分离效果及较低的基线噪音，所以最终选择了 Phenomenex F5 作为本实验的分离色谱柱。

对比了5种流动相体系：5 mM乙酸胺水/5 mM乙酸胺甲醇、5 mM乙酸胺水/甲醇、2 mM乙酸胺水/甲醇、0.01%甲酸水/乙腈、 2 mM乙酸胺水/乙腈。发现PFOPA 、 PFDPA等膦酸只有在2 mM MH_4Ac中有色谱峰，对流动相pH敏感；FTOH类物质在甲醇体系中基线低于乙腈体系；所以最终选择了2 mM乙酸胺水/甲醇作为本实验的流动相。优化后的色谱图如图1所示。

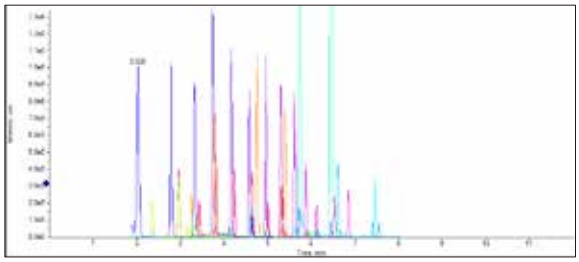

图1. 56种PFASs提取离子流图

2.2 56种PFASs线性

用30%甲醇水配置混合梯度标准曲线，各化合物在各自的浓度范围内均线性良好，R > 0.995（见表3）。

2.3 数据重现性

用自来水配置50 ng/L的基质标样，连续进样6针，56种PFASs峰面积的RSD在5%以内，表明该检测方法重现性良好，数据稳定可靠。（见图2）

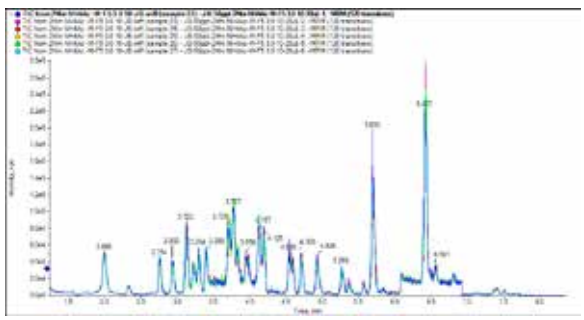

图2. 连续进样6针数据重现性

内容提要

表2. 离子对信息表

序号	化合物	简写	母离子 (m/z)	子离子 (m/z)	保留时间（min）	去簇电压(V)	碰撞能量(eV)
1	全氟丁酸	PFBA	213	168.9	1.9	-30	-11
2	全氟戊酸	PFPeA	263	218.9	2.8	-30	-11
			263	63	2.8	-30	-29
3	全氟己酸	PFHxA	312.9	268.9	3.4	-35	-13
			312.9	119	3.4	-35	-26
4	全氟庚酸	PFHpA	362.9	318.9	3.8	-35	-15
			362.9	168.9	3.8	-35	-21
5	全氟辛酸	PFOA	412.9	368.9	4.2	-35	-15
			412.9	168.9	4.2	-35	-25
6	全氟壬酸	PFNA	462.9	418.9	4.7	-40	-14
			462.9	218.9	4.7	-40	-23
7	全氟癸酸	PFDA	512.9	468.9	5.1	-60	-16
			512.9	218.9	5.1	-60	-24
8	全氟十一酸	PFUdA	562.9	518.9	5.4	-60	-19
			562.9	268.9	5.4	-60	-26
9	全氟十二酸	PFDoA	612.8	568.8	5.7	-60	-19
			612.8	168.9	5.7	-60	-31
10	全氟十三酸	PFTrDA	662.8	618.8	6	-60	-17
			662.8	168.9	6	-60	-34
11	全氟十四酸	PFTeDA	712.8	668.8	6.2	-30	-17
			712.8	168.9	6.2	-30	-37
12	全氟十六酸	PFHxDA	813	768.9	6.6	-70	-20
			813	168.9	6.6	-70	-35
13	全氟十八酸	PFODA	913	868.9	6.9	-70	-22
			913	168.9	6.9	-70	-38
14	全氟丁基磺酸	PFBS	298.9	80	3	-70	-60
			298.9	99	3	-70	-48
15	全氟戊基磺酸	PFPeS	349	80	3.5	-80	-80
			349	99	3.5	-80	-80
16	全氟己基磺酸	PFHxS	398.9	80	3.9	-70	-80
			398.9	99	3.9	-70	-80
17	全氟庚基磺酸	PFHpS	448.7	79.9	4.3	-100	-85
			448.7	98.9	4.3	-100	-80
18	全氟辛基磺酸	PFOS	498.9	80	4.7	-60	-100
			498.9	99	4.7	-60	-95
19	全氟壬基磺酸	PFNS	549	80	5.1	-80	-100
			549	99	5.1	-80	-95
20	全氟癸基磺酸钠	PFDS	598.8	79.9	5.4	-100	-100
			598.8	98.9	5.4	-100	-100
21	全氟十二烷磺酸	PFDoS	699	80	6	-80	-115
			699	99	6	-80	-100
22	N-甲基全氟辛烷氨基乙酸	N-MeFOSAA	570	419	5.4	-40	-27
			570	218.9	5.4	-40	-34
23	N-乙基全氟辛烷氨基乙酸	N-EtFOSAA	584	419	5.5	-40	-27
			584	219	5.5	-40	-35
24	全氟2-甲基-3-氧杂己酸	HFPO-DA	328.9	185	3.5	-5	-32
			328.9	169	3.5	-5	-17
25	4,8-二噁-3H全氟壬酸乙酯	NaDONA	376.9	251	3.9	-10	-14
			376.9	84.9	3.8	-10	-34
26	2-[(6-氯-1,1,2,2,3,3,4,4,5,5,6,6-十二氟己基)氧基]-1,1,2,2-四氟乙烷磺酸	9Cl-PF3ONS	530.9	351	4.8	-50	-36
			530.9	83	4.8	-50	-70
27	2-[(8-氯-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-十六氟辛基)氧基]-1,1,2,2-四氟乙烷磺酸	11Cl-PF3OUdS	630.9	450.8	5.5	-50	-41
			630.9	83	5.5	-50	-84
28	全氟-3,6-二噁庚酸	3,6-OPFHpA	295	85	3.3	-5	-38
			295	201	3.3	-5	-10
29	全氟(2-乙氧基乙烷)磺酸	PFEESA	314.9	83	3.2	-30	-23
			314.9	134.9	3.2	-30	-30
30	2,2,3,3-四氟-3-(三氟甲氧基)丙酸	PF4OPeA	228.9	84.9	2.3	-5	-13
			228.9	184.9	2.3	-5	-9
31	2,2,3,3,4,4-六氟-4-(三氟甲氧基)丁酸	PF5OHxA	278.9	85	3	-5	-13
			278.9	235	3	-5	-9
32	全氟己烷膦酸	PFHxPA	399	78.8	2.4	-26	-68
33	全氟辛基膦酸	PFOPA	499	78.9	3.6	-75	-107
34	全氟癸基膦酸	PFDPA	599	79.2	4.4	-100	-102
35	6-氯全氟辛基膦酸	Cl-PFOPA	515	79	3.6	-100	-92
36	1H,1H,2H,2H-全氟辛基膦酸	6:2PAP	443	97	4.1	-63	-31
			443	79.1	4.1	-63	-83
37	1H,1H,2H,2H-全氟癸基膦酸	8:2PAP	542.8	78.9	4.9	-35	-87
			542.8	97	4.9	-35	-20
38	双1H,1H,2H,2H-全氟辛基次膦酸	6:2diPAP	789	96.8	6.1	-80	-85
			789	79.1	6.1	-80	-100
39	双1H,1H,2H,2H-全氟癸基次膦酸	8:2diPAP	988.7	542.8	6.7	-100	-34
			988.7	79.1	6.7	-100	-100
40	1H,1H,2H,2H-全氟己基磺酸	4:2FTS	326.9	306.8	3.3	-50	-29
			326.9	81.1	3.3	-50	-52
41	1H,1H,2H,2H-全氟辛基磺酸	6:2FTS	426.8	407	4.2	-20	-34
			426.8	80.9	4.2	-20	-74
42	1H,1H,2H,2H-全氟癸基磺酸	8:2FTS	526.9	506.8	5.1	-50	-37
			526.9	80.9	5.1	-50	-84
43	1H,1H,2H,2H-全氟十二烷基磺酸	10:2FTS	626.8	606.8	5.7	-80	-44
			626.8	80.9	5.7	-80	-108
44	6:2氟调聚醇	6:2 FTOH	423	59	6.5	-10	-55
			409	45	6.5	-10	-55
45	7:2s氟调聚醇	7:2sFTOH	473	59	5.8	-10	-60
			459	45	5.8	-10	-60
46	8:2氟调聚醇	8:2 FTOH	523	59	7.3	-10	-60
			509	45	7.3	-10	-60
47	N-甲基全氟辛基磺酰胺	N-MeFOSE	616	59	7.5	-20	-70
			602	45	7.5	-20	-70
48	六氟环氧丙烷三聚酸	HFPO-TA	495	185	4.7	-20	-13
			495	119	4.7	-20	-55
49	PF8O3A2	PF8O3A2	437.1	229.1	2.3	-50	-30
			437.1	323	2.3	-50	-20
50	全氟辛烷	FOSA-I	497.8	77.9	6.7	-30	-95
			497.8	477.8	6.7	-30	-34
51	N-乙基全氟辛烷磺酰胺	N-EtFOSA-M	526	168.9	7.6	-58	-38
			526	218.9	7.6	-58	-33
52	N-甲基全氟辛烷磺酰胺	N-MeFOSA-M	511.9	168.9	7.5	-30	-36
			511.9	218.9	7.5	-30	-34
53	双（全氟氧基）膦酸钠	6:6 PFPi	700.9	400.8	5.8	-27	-72
			700.9	62.9	5.8	-27	-100
54	全氟氧基全氟辛基膦酸钠	6:8 PFPi	800.9	400.9	6.2	-30	-72
			800.9	500.8	6.2	-30	-74
55	双全氟辛基磷酸钠	8:8 PFPi	900.7	500.8	6.5	-20	-90
			900.7	63	6.5	-20	-110
56	8Cl-全氟辛烷磺酸	8Cl-PFOS	514.8	79.9	4.7	-30	-100
			514.8	98.9	4.7	-30	-97

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内容提要

表3. 56种PFASs线性

化合物	线性方程	线性相关系数R
全氟丁酸	y = 3515.05872 x + 8002.67651	0.9981
全氟戊酸	y = 2569.54696 x + -2570.21092	0.9984
全氟己酸	y = 2489.48096 x + 435.51481	0.9984
全氟庚酸	y = 853.80127 x + -10.54984	0.9982
全氟辛酸	y = 2718.40116 x + 1385.19442	0.9984
全氟壬酸	y = 2073.37451 x + 841.74242	0.9975
全氟癸酸	y = 2003.70900 x + -10544.80924	0.9977
全氟十一酸	y = 2378.52760 x + -11132.26691	0.9982
全氟十二酸	y = 1128.29378 x + -3469.39832	0.9992
全氟十三酸	y = 451.98726 x + -1596.52227	0.9996
全氟十四酸	y = 241.42394 x + -110.49558	0.9968
全氟十六酸	y = 370.65285 x + -1888.65291	0.9970
全氟十八酸	y = 657.49261 x + -3234.98359	0.9980
全氟丁基磺酸	y = 989.06533 x + -870.66196	0.9982
全氟戊基磺酸	y = 548.65111 x + -55.91373	0.9993
全氟己基磺酸	y = 1119.24435 x + -1360.26422	0.9995
全氟庚基磺酸	y = 1046.85192 x + -209.21200	0.9993
全氟辛基磺酸	y = 953.41827 x + -1090.09682	0.9989
全氟壬基磺酸	y = 491.19456 x + -2133.37450	0.9978
全氟癸基磺酸钠	y = 615.49043 x + -2285.34154	0.9983
全氟十二烷磺酸	y = 45.43087 x + -464.33428	0.9962
N-甲基全氟辛烷氨基乙酸	y = 132.89396 x + -942.11004	0.9981
N-乙基全氟辛烷氨基乙酸	y = 107.87458 x + -935.39497	0.9980
全氟2-甲基-3-氧杂己酸	y = 1022.95149 x + -1389.43751	0.9993
4,8-二噁-3H全氟壬酸乙酯	y = 1916.82995 x + 18.95185	0.9993
2-[(6-氯-1,1,2,2,3,3,4,4,5,5,6,6-十二氟己基)氧基]-1,1,2,2-四氟乙烷磺酸	y = 2273.02959 x + -520.09503	0.9971
2-[(8-氯-1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-十六氟辛基)氧基]-1,1,2,2-四氟乙烷磺酸	y = 1339.70388 x + -6009.99228	0.9988
全氟-3,6-二噁庚酸	y = 650.15912 x + -547.64947	0.9984
全氟(2-乙氧基乙烷)磺酸	y = 4536.53500 x + -4452.91217	0.9984
2,2,3,3-四氟-3-(三氟甲氧基)丙酸	y = 554.19388 x + -340.83664	0.9990
2,2,3,3,4,4-六氟-4-(三氟甲氧基)丁酸	y = 906.14119 x + -183.36351	0.9989

化合物	线性方程	线性相关系数R
全氟己烷膦酸	y = 52.97514 x + 398.72113	0.9978
全氟辛基膦酸	y = 49.69305 x + -333.66180	0.9979
全氟癸基膦酸	y = 35.00773 x + 583.34232	0.9966
6-氯全氟辛基膦酸	y = 49.47567 x + -588.28676	0.9986
1H,1H,2H,2H-全氟辛基膦酸	y = 124.87604 x + -951.15764	0.9979
1H,1H,2H,2H-全氟癸基膦酸	y = 19.86421 x + 1111.48160	0.9981
双1H,1H,2H,2H-全氟辛基次膦酸	y = 56.31375 x + -1335.57306	0.9963
双1H,1H,2H,2H-全氟癸基次膦酸	y = 32.40469 x + 364.84337	0.9957
1H,1H,2H,2H-全氟己基磺酸	y = 207.54971 x + 248.17934	0.9988
1H,1H,2H,2H-全氟辛基磺酸	y = 154.86056 x + 808.06289	0.9985
1H,1H,2H,2H-全氟癸基磺酸	y = 116.01455 x + -606.84540	0.9975
1H,1H,2H,2H-全氟十二烷基磺酸	y = 103.83525 x + -3972.32213	0.9985
6:2氟调聚醇	y = 13604.53160 x + -6534.99534	0.9983
7:2s氟调聚醇	y = 7491.16557 x + 10736.55787	0.9958
8:2氟调聚醇	y = 45.24992 x + 6270.36124	0.9991
N-甲基全氟辛基磺酰胺	y = 851.82814 x + -4204.31790	0.9993
六氟环氧丙烷三聚酸	y = 335.87535 x + -1598.05250	0.9962
PF8O3A2	y = 84.66145 x + -236.53582	0.9992
全氟辛烷	y = 984.46938 x + -1083.88020	0.9991
N-乙基全氟辛烷磺酰胺	y = 193.96445 x + -751.49672	0.9996
N-甲基全氟辛烷磺酰胺	y = 198.22802 x + -741.17681	0.9990
双（全氟氧基）膦酸钠	y = 446.91796 x + -3374.32565	0.9993
全氟氧基全氟辛基膦酸钠	y = 78.57728 x + -602.57270	0.9971
双全氟辛基磷酸钠	y = 111.13986 x + -233.77574	0.9964
8Cl-全氟辛烷磺酸	y = 312.45772 x + -710.53661	0.9986
全氟丁酸	y = 3515.05872 x + 8002.67651	0.9981
全氟戊酸	y = 2569.54696 x + -2570.21092	0.9984
全氟己酸	y = 2489.48096 x + 435.51481	0.9984
全氟庚酸	y = 853.80127 x + -10.54984	0.9982
全氟辛酸	y = 2718.40116 x + 1385.19442	0.9984
全氟壬酸	y = 2073.37451 x + 841.74242	0.9975
全氟癸酸	y = 2003.70900 x + -10544.80924	0.9977
全氟十一酸	y = 2378.52760 x + -11132.26691	0.9982

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内容提要

3.总结

本文使用SCIEX Triple Quad™系统建立了LC-MS/MS方法测定饮用水中56种PFASs的快速检测方法。该方法采用甲醇稀释后直接进样，无需复杂的前处理过程，极大节约时间和经济成本。该方法灵敏度高，数据重现性好，可应用于实际水样的批量测定。

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内容提要

水中六溴环十二烷和四溴双酚A的快速分析检测

Rapid Determination of Hexabromocyclododecane and Tetrabromobisphenol A in Water

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Key words: HBCDs; TBBPA; LC-MS/MS; Water; QTRAP 4500

引言

六溴环十二烷（hexabromocyclododecane, HBCDs）和四溴双酚A（tetrabromobisphenol A, TBBPA）是目前全球应用最为广泛的两种溴系阻燃剂，大量应用于纺织、家电和工业品中。HBCDs被认定是一种持久性有机污染物（POPs），具有持久性、迁移性、生物蓄积性，并且可导致血清甲状腺激素浓度下降、抑制神经递质正常吸收、引起肝组织病理学改变，且具有致畸、致癌潜力，因此，HBCDs正受到国际社会的广泛关注，欧盟在《关于在电子电气设备中限制使用某些有害物质指令（RoHS）》中将HBCDs定为管控物质；欧洲化学品管理（ECHA）将HBCDs归类为高关注度物质；同时持久性有机污染物审查委员会第六次会议通过了对HBCDs风险简介草案的审查。TBBPA是一种类似于持久性有机污染物潜在环境内分泌干扰物，能在环境和生物体内累积，对环境和生物体产生严重影响，已有研究表明TBBPA对藻类、软体动物、甲壳动物和鱼体有明显的毒性作用。

HBCDs有三种主要异构体，在160 ℃以上会发生热重排，在240 ℃以上将脱溴降解，因此，不适用于气相及气相质谱法。TBPPA的极性大于HBCDs，在进行前处理和液相色谱分离是，TBBPA均表现出比HBCDs较强的亲水性，所以在前处理的SPE柱选择和液相色谱梯度设置，均需要兼顾二者的回收率和保留问题。因此，需要开发快速、高选择性、准确定量，适用于HBCDs和TBBPA的检测方法。

本实验的优势和特点

1、快速高通量，采用ESI负模式扫描，一针5 min内完成TBBPA和HBCDs三个异构体的准确定性和定量。

2、灵敏度高，HBCDs的三个异构体线性范围为0.001-1 ng/mL，TBBPA的线性范围为0.005-1 ng/mL，r值均为0.995以上。

3、准确度好，考察了自来水中HBCDs的0.001 ng/mL、0.01ng/mL和1 ng/mL三个浓度，以及TBBPA的0.005 ng/mL和0.01 ng/mL和1 ng/mL的三个浓度，添加回收率均在85.5%-94.6%之间。

4、重现性好，三个不同浓度下的多份质控样本的RSD在1.8%-3.9%范围内。

5、前处理方法简单，水样经过SPE浓缩后上样，快速易操作。

实验方法

1、样品前处理

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内容提要

取100 mL水样，调节pH至2-3，过Cleanert PEP固相萃取柱后，用二氯甲烷淋洗，在氮吹仪上吹干后，用初始流动相定容至1 mL。转入自动进样小瓶中待测[1]。

2、液相方法

色谱柱：Phenomenex C18, 2.6 μm, 3.0 mm × 50 mm

流动相：A：水（0.02%氨水）
B：乙腈：甲醇（15:85）

进样量：10 μL

梯度洗脱程序：如表1所示

表1. 液相梯度设置。

Time/min	A/%	B/%
0.00	95	5
0.20	60	40
0.50	15	85
3.00	15	85
3.1	95	5
5	95	5

3、质谱方法

质谱仪器：SCIEX QTRAP® 4500系统

扫描方式： MRM采集模式，负离子扫描

离子源：ESI源

离子源参数：

IS电压: -4500 V　　源温度 TEM: 200 ℃

气帘气 CUR: 30 psi　　碰撞气 CAD: Medium

雾化气 GS1: 45 psi　　辅助气 GS2: 60 psi

离子对参数如表2所示。

表2. 化合物离子对参数。

Compound	Q1	Q3	ID	RT(min)	DP	CE
α-HBCDs	640.6	79.0	α-HBCDs 1	1.74	-122	-50
	640.6	81.0	α-HBCDs 2	1.74	-122	-50
β-HBCDs	640.6	79.0	β-HBCDs 1	1.87	-122	-50
	640.6	81.0	β-HBCDs 2	1.87	-122	-50
γ-HBCDs	640.6	79.0	γ-HBCDs 1	1.98	-122	-50
	640.6	81.0	γ-HBCDs 2	1.98	-122	-50
α-HBCDs-13C12	652.6	79.0	α-HBCDs-13C12	1.74	-130	-50
β-HBCDs-13C12	652.6	79.0	β-HBCDs-13C12	1.87	-130	-50
γ-HBCDs-13C12	652.6	79.0	γ-HBCDs-13C12	1.98	-130	-50
TBBPA	542.6	417.5	TBBPA 1	0.80	-130	-55
	542.6	445.6	TBBPA 2	0.80	-130	-44

结果与讨论

1、总离子流图如图2所示，HBCDs的三个异构体均很好的分离，且保证了TBBPA良好的峰形。

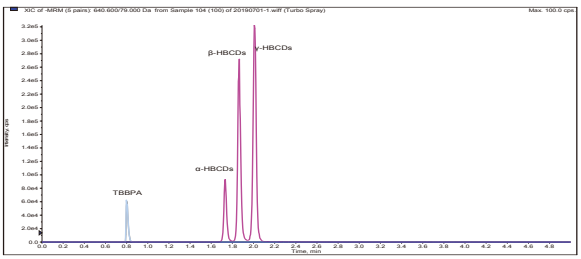

图2. HBCDs的三种异构体和TBBPA的总离子流图。

2、自来水样本前处理回收率：

配置HBCDs浓度为0.001 ng/mL、0.01 ng/mL和1 ng/mL，且分别含有TBBPA的浓度为0.005 ng/mL和0.01 ng/mL和1 ng/mL的三个自来水质控样本，按照样本前处理操作，每批次浓度三份，计算回收率，结果如表3所示：

表3. 自来水样本前处理回收率。

自来水加标回收率/%			
	0.001 ng/mL	0.01 ng/mL	1 ng/mL
α -HBCDs	88.0	93.9	89.5
β -HBCDs	87.2	88.6	90.6
γ -HBCDs	92.1	90.6	94.6
TBBPA	85.5	87.4	92.2
自来水加标回收率/%			
	0.005 ng/mL	0.01 ng/mL	1 ng/mL
TBBPA	85.5	87.4	92.2

3、方法定量下限:

自来水中HBCDs的定量下限为0.001 ng/mL，TBBPA的定量下限为0.005 ng/mL。

4、方法重现性:

配置HBCDs浓度为0.001 ng/mL、0.01 ng/mL和1 ng/mL的质控样本，且TBBPA的浓度分别为0.005 ng/mL和0.01 ng/mL和1 ng/mL的三个浓度的自来水质控样本，按照样本前处理进行操作，每个浓度批次重复三次，计算相对标准偏差RSD，结果如下表所示：

表4. 方法重现性。

三个不同浓度重复三次RSD/%			
	0.001 ng/mL	0.01 ng/mL	1 ng/mL
α -HBCDs	3.2	2.3	3.0
β -HBCDs	3.8	2.9	2.4
γ -HBCDs	3.1	2.0	1.8
三个不同浓度重复三次RSD/%			
	0.005 ng/mL	0.01 ng/mL	1 ng/mL
TBBPA	3.9	3.2	2.6

5、基质样品线性范围

在自来水样品中，HBCDs的三个异构体在0.001-1 ng/mL的线性关系良好，r>0.995，TBPPA在0.005-1 ng/mL的线性关系为r= 0.99699 ，保证了不同浓度样品的定量准确性。

表5. 基质样品线性范围。

序号	中文名	线性范围(ng/mL)	相关系数r
1	α -HBCDs	0.001-1	0.99745
2	β -HBCDs	0.001-1	0.99706
3	γ -HBCDs	0.001-1	0.99899
4	TBBPA	0.005-1	0.99699

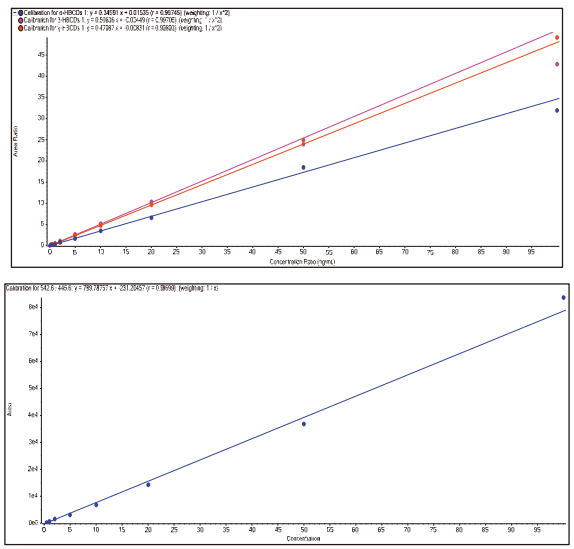

图3. HBCDs的三种异构体和TBBPA的线性关系图。

实际样本的检测

测试北京朝阳区自来水中HBCDs和TBBPA的含量，按照5中样品前处理过程操作，未检测出HBCDs和TBBPA。

RUO-MKT-02-9998-ZH-A

内容提要

总结

1、 本文采用了SCIEX QTRAP 4500系统，建立了快速检测水中的HBCDs三种异构体和TBBPA方法；

2、 SCIEX专利技术的TurboV™离子源，专利离子源主动排废技术和极强的抗污染能力，保证了日常大批量样本检测的高灵敏度、稳定性和耐用性。

3、 SCIEX专利的脉冲技术检测器技术，不仅具有更好的负离子灵敏度，且保证了质控样品和标准曲线在低浓度点的定量准确定和稳定性。

参考文献：

[1] 章勇，张蓓蓓，穆肃，等. 液质联用法测定水中六溴环十二烷和四溴双酚A[J]. 环境科学与技术: 2014,37(4):107-112.

RUO-MKT-02-9998-ZH-A

内容提要

SCIEX LC-MS/MS系统对纺织品中11种有机磷阻燃剂同时定量分析

Simultaneous Quantitative Analysis of 11 Orgnophosphorus Flame Retardant in Textile by SCIEX LC-MS/MS

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关键词： Orgnophosphorus Flame retardant, textile, LC-MS/MS

有机磷阻燃剂（Orgnophosphorus Flame retardant, OPFRs）是与卤系阻燃剂并重的一类阻燃剂，广泛应用于玩具、建材、纺织、塑料、化工以及电子等行业。其性质十分稳定，具有生物累积性，长期接触会对人产生危害。许多国家和地区颁布法律法规以限制OPFRs在各种产品中的使用，其中明令禁止在纺织品中使用的有 6 种，随着 OPFRs 毒理学、环境化学等的深入研究，各国对其使用、管理法规将日趋严格，未来可能有更多 OPFRs 列入限用禁用范围。因此，建立纺织品中多种OPFRs 快速测定方法对纺织品质量保证体系建设及健康环境建立具有重要意义。本文利用SCIEX ExionLC™系统和SCIEX Triple Quad™ 3500系统建立了纺织品中11种有机磷阻燃剂的LC-MS/MS解决方案。

本实验方法具有如下特点：

- 高通量，一针进样8分钟，可同时测定11种OPFRs残留并准确定量。
- 线性关系良好，在各自的浓度范围内，线性相关系数R >0.995。
- 前处理方法简单高效，3个添加水平的平均回收率在80.2%~99.6%之间。
- 方法灵敏度高，11种OPFRs定量限浓度为0.1 ~5 ng/mL。

1.实验部分

1.1样品前处理

称取5.0 g样品置于50 mL具塞萃取瓶中，用剪刀剪成约5 mm × 5 mm的碎片，加入20 mL甲醇，50 ℃超声提取30 min，冷却至室温后过0.22 μm滤膜，LC-MS/MS进样分析。

1.2 色谱条件

色谱柱：Phenomenex Kinetex, C18 (2.6 μm, 2.1 × 100 mm)

流动相：A相：水（含5 mM甲酸铵）
B相：甲醇

流速：0.4 mL/min

进样量：10 μL

洗脱程序：梯度洗脱（表1）

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内容提要

表1. 液相洗脱程序

时间（min）	A 相(%)	B 相(%)
0.0	90	10
1.0	90	10
4.0	10	90
6.0	10	90
6.1	90	10
8.0	90	10

1.3 质谱条件

离子源：电喷雾电离（electrospray ionization, ESI），正离子模式

离子源参数

气帘气: 30 psi；　　源温度: 550℃；

碰撞气: 中；　　喷雾气: 55 psi；

辅助加热气: 60 psi

离子对信息（表2）

表2. 离子对信息表

化合物	母离子(m/z)	子离子(m/z)	去簇电压(V)	碰撞电压(V)
2,2-二(氯甲基)-1,3-丙二醇 双[双(2-氯乙基)]磷酸酯1	583	361	127	28
2,2-二(氯甲基)-1,3-丙二醇 双[双(2-氯乙基)]磷酸酯2	583	235.1	127	45
磷酸叔丁基苯二苯酯 1	383.1	327.1	129	29
磷酸叔丁基苯二苯酯 2	383.1	57.1	129	50
磷酸苯基(二叔丁基苯基)酯 1	439.2	327.1	160	38
磷酸苯基(二叔丁基苯基)酯 2	439.2	383.1	160	30
邻磷酸三甲酚酯 1	369.1	166	160	37
邻磷酸三甲酚酯 2	369.1	91	160	51
磷酸三(2-氯丙基)酯 1	327	99	75	28
磷酸三(2-氯丙基)酯 2	327	215	75	38
磷酸三(1,3-二氯异丙基)酯 1	431.1	99	90	42
磷酸三(1,3-二氯异丙基)酯 2	431.1	209	90	23
磷酸三(2-氯乙基)酯 1	286.1	99	80	31
磷酸三(2-氯乙基)酯 2	286.1	161.1	80	22
磷酸三(2,3-二溴丙基)酯 1	698.6	99	120	51
磷酸三(2,3-二溴丙基)酯 2	698.6	299	120	23
磷酸三甲酯 1	141	108.9	74	23
磷酸三甲酯 2	141	127	74	23
磷酸三对甲苯酯 1	369.2	166.1	160	40
磷酸三对甲苯酯 2	369.2	91.1	160	56
磷酸三苯酯 1	327.2	77	130	57
磷酸三苯酯 2	327.2	153.2	130	33

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内容提要

2.实验结果

2.1 11 种OPFRs提取离子流图

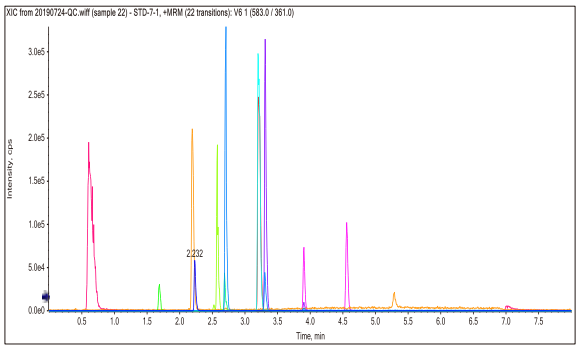

图1. 11种OPFRs提取离子流图

2.2 11 种OPFRs线性及定量限

用甲醇配置混合梯度标准曲线，各化合物在各自的浓度范围内均线性良好，R > 0.995，定量限在0.1~5 ng/mL范围内（见表3）。

2.3 加标回收率

在空白棉布、聚酯纤维两种基质样本中分别添加高、中、低三个浓度水平的混合标准品，每个浓度平行测定5次，得到三个添加浓度的平均回收率在80.2%~99.6%范围内，5针平行样品的RSD %在2.7-8.9 %，回收率和RSD %均满足测试要求。见表4。

表3. 11种OPFRs线性及定量限

化合物	浓度范围 (ng/mL)	线性方程	线性相关系数R	定量限(ng/mL)
2,2-二(氯甲基)-1,3-丙二醇 双[双(2-氯乙基)]磷酸酯	1~100	y = 1025.85105 x - 195.05126	0.99843	1
磷酸叔丁基苯二苯酯	0.1~10	y = 6.26504e4 x - 233.62176	0.99783	0.1
磷酸苯基(二叔丁基苯基)酯	0.1~10	y = 13421.15024 x + 64.84870	0.99885	0.1
邻磷酸三甲酚酯	1~100	y = 8286.47401 x + 548.45769	0.99728	1
磷酸三(2-氯丙基)酯	1~100	y = 5144.68601 x + 3901.11374	0.99772	1
磷酸三(1,3-二氯异丙基)酯	1~100	y = 3135.03954 x + 3993.52836	0.99820	1
磷酸三(2-氯乙基)酯	5~500	y = 116.71352 x + 128.77961	0.99851	5
磷酸三(2,3-二溴丙基)酯	5~500	y = 139.92963 x + 151.10176	0.99549	5
磷酸三甲酯	1~100	y = 10322.73970 x + 2574.78073	0.99809	1
磷酸三对甲苯酯	1~100	y = 8771.08395 x - 351.27998	0.99779	1
磷酸三苯酯	1~100	y = 5147.02355 x - 339.29865	0.99546	1

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内容提要

表4. 回收率测试结果

化合物	棉布		聚酯纤维	
	添加浓度(ng/g)	平均回收率%	添加浓度(ng/g)	平均回收率%
2,2-二(氯甲基)-1,3-丙二醇 双[双(2-氯乙基)]磷酸酯	10;40;200	84.9; 86.9;89.3	10;40;200	82.9; 84.6;90.4
磷酸叔丁基苯二苯酯	1;4;20	80.2;85.6;92.1	1;4;20	82.3;86.9;93.5
磷酸苯基(二叔丁基苯基)酯	1;4;20	81.5;84.6;84.8	1;4;20	82.5;87.2;86.5
邻磷酸三甲酚酯	10;40;200	86.3; 82.9;90.4	10;40;200	85.2; 87.6;97.2
磷酸三(2-氯丙基)酯	10;40;200	81.6; 85.2;94.1	10;40;200	82.2; 87.9;87.6
磷酸三(1,3-二氯异丙基)酯	10;40;200	88.2; 87.2;95.2	10;40;200	85.2; 83.9;92.6
磷酸三(2-氯乙基)酯	50;200;1000	81.5;84.1;90.2	50;200;1000	88.2.;83.1;88.4
磷酸三(2,3-二溴丙基)酯	50;200;1000	82.6;89.3;85.9	50;200;1000	85.7;93.2;98.6
磷酸三甲酯	10;40;200	89.3; 88.2;93.2	10;40;200	87.4; 87.9;97.6
磷酸三对甲苯酯	10;40;200	85.8; 88.2;94.4	10;40;200	82.2; 83.7;90.6
磷酸三苯酯	10;40;200	82.4; 89.3;98.1	10;40;200	82.8; 83.9;99.6

3.样品测试

取布料按照上面方法进行测试，结果显示有部分OPFRs检出。

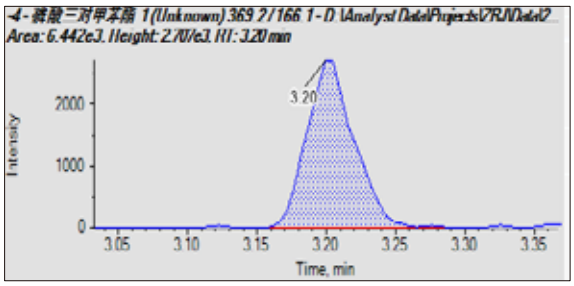

图2. 实际样品中磷酸三对苯甲酯检测图谱

4.总结

本文使用SCIEX Triple Quad™ 3500系统建立了LC-MS/MS方法测定纺织品中11种OPFRs的定量检测方案，包括样品前处理、数据采集和数据处理等。该方法前处理简单，进样一针8 min内全部出峰，分析时间短。化合物在各自的线性范围内线性关系良好，相关系数大于0.998。方法灵敏度高，可应用于实际样品的批量测定。

RUO-MKT-02-12540-ZH-A

内容提要

SCIEX LC-MS/MS系统快速定量饮用水中4种氯酚类化合物

Rapid Identification and Quantification of Four Chlorophenols in Drinking Water by SCIEX LC-MS/MS System

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Keywords: LC-MS/MS, Chlorophenols, Drinking Water

氯化法消毒因经济实惠、效果好而常被用于饮用水的消毒，但消毒过程中，水中的酚类物质易被氧化生成氯酚类化合物。氯酚类化合物在环境中难以降解，在生物体内容易蓄积，即使含量极低，也可导致生物的内分泌失调，具有致畸、致癌、致基因突变的潜在毒性。所以在将发布的GB/T 5750《生活饮用水标准检验方法》中给出了2,4,6-三氯酚和五氯酚的检测方法，并在《生活饮用水卫生标准》（GB 5749-2022）明确规定了饮用水中2,4,6-三氯酚和五氯酚的浓度限值为200 µg/L和9 µg/L。

本实验采用SCIEX LC-MS/MS系统（图1）并基于新GB/T 5750《生活饮用水标准检验方法》建立了4种氯酚类化合物的LC-MS/MS定量解决方案。结果显示，4种氯酚类化合物的定量限在0.5 µg/L以下，完全满足《生活饮用水卫生标准》（GB 5749-2022）的限量要求。

图1. SCIEX LC-MS/MS系统

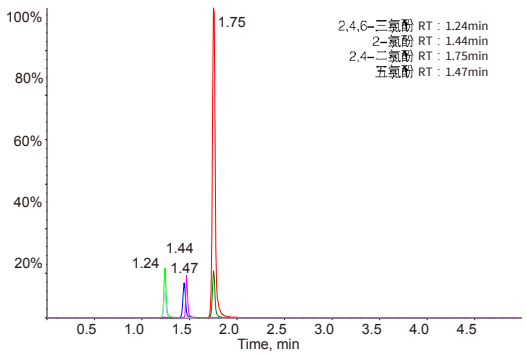

图2. 4种氯酚类化合物色谱图

本实验方法具有如下特点：

- 时间短，5分钟完成4种氯酚类化合物分析（图2）。
- 灵敏度高，无须浓缩、直接进样，完全满足《生活饮用水卫生标准》（GB 5749-2022）的限量要求。

RUO-MKT-02-14914-ZH-A

内容提要

1. 样品前处理

取适量自来水过膜后上机测试。

2. 实验方法

2.1 液相方法

液相：SCIEX ExionLC™ 系统

色谱柱：Phenomenex Gemini NX-C18, 30 × 2.0 mm, 3 µm

流动相：A相：水（含5 mM NH_4HCO_3） B相：乙腈

流速：0.5 mL/min

进样量：20 µL

洗脱程序：梯度洗脱（表1）

表1. 液相洗脱程序

时间（分钟）	A 相(%)	B 相(%)
0.0	90	10
2.0	35	65
2.1	10	90
3.0	10	90
3.1	90	10
5.0	90	10

2.2 质谱方法

电离模式：大气压化学电离（atmospheric pressure chemical ionization , APCI），负离子模式。

离子源参数：

气帘气：30 psi；　　源温度：400℃；

碰撞气：8；　　喷雾气：55 psi；

针电流：-3 µA。

离子对信息（表2）

表2. 离子对信息表

母离子	子离子	离子名称	去簇电压（V）	碰撞能量（V）
194.9	35.0	2,4,6-Trichlorophenol 1	-70	-49
196.9	35.0	2,4,6-Trichlorophenol 2	-70	-49
127.0	35.0	2-Chlorophenol 1	-60	-28
127.0	127.0	2-Chlorophenol 2	-80	-9
161.0	125.0	2,4-Dichlorophenol 1	-60	-21
163.0	124.9	2,4-Dichlorophenol 2	-60	-21
264.9	35.0	Pentachlorophenol 1	-70	-45
262.9	35.0	Pentachlorophenol 2	-70	-45

3.实验结果

3.1 线性

4种氯酚类在0.5 µg/L-100 µg/L有良好的的线性（图3）。相关系数R^2 > 0.995。

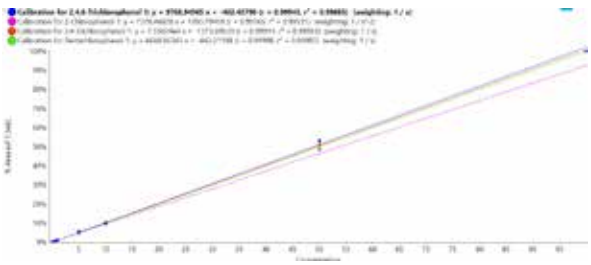

图3. 4种氯酚类化合物线性图

3.2 灵敏度

0.5 µg/L自来水加标浓度下4种氯酚类化合物色谱图（图4）。结果显示，四种氯酚类化合物灵敏度高，轻松应对标准要求。

RUO-MKT-02-14914-ZH-A

内容提要

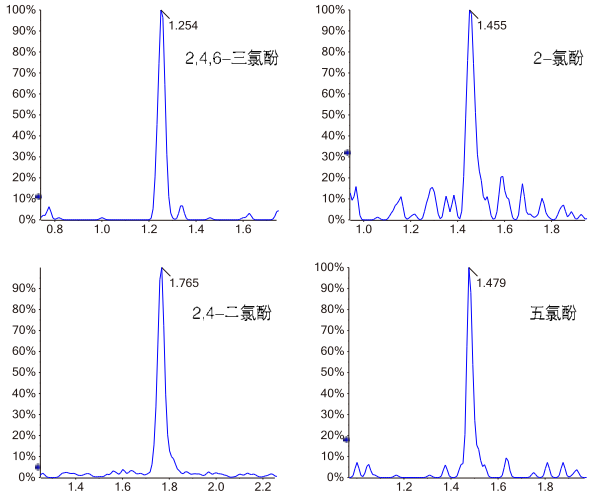

图4. 0.5 µg/L加标浓度下4种氯酚类化合物色谱图

4.总结

从实验结果看，SCIEX LC-MS/MS 灵敏度高，4种氯酚类化合物完全满足《生活饮用水卫生标准》（GB 5749-2022）的限量要求。

RUO-MKT-02-14914-ZH-A

内容提要

Simple and rapid quantification of per- and polyfluoroalkyl substances (PFAS) in seawater

Using the SCIEX 7500 system

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[1]SCIEX, UK; [2]SCIEX, The Netherlands; [3]SCIEX, Germany

In this technical note, a method is presented for quantifying per- and polyfluoroalkyl compounds (PFAS) in seawater at the low ng/L range using a simple sample preparation approach, with no solid phase extraction (SPE). The sensitivity of the SCIEX 7500 system[1] allowed for the ultra-trace level quantification of PFAS in un-spiked seawater samples using only direct injection analysis.

With seafood consumption identified as a major pathway for human exposure to PFAS, and PFAS regulations continuously tightening as concerns about exposure rise, the ability to monitor PFAS levels in seawater has become critical. The ocean has been referred to as a "terminal sink" for PFAS, with perfluorooctane sulfonate (PFOS), perfluorohexanoic acid (PFHxA) and perfluorooctanoic acid (PFOA) reported as being abundant in surface and subsurface seawater.[2] While recent advancements suggest that petrochemicals released into the sea could be one source of PFAS in seawater,[3] the distribution and abundance of PFAS in seawater is still poorly understood.[2]

Previous analytical methods from SCIEX have enabled the detection of low ng/L levels for various PFAS compounds in drinking water and surface water to help meet European Union regulatory requirements.[4,5,6] Seawater is a very difficult matrix to analyze due to the high salt levels which typically results in poor quantification due to high matrix effects. Here, we provide a robust and sensitive method for quantifying PFAS in seawater using external standards and a standard addition workflow.

Key features of PFAS analysis using the SCIEX 7500 system

- Simple, reproducible and robust sample preparation was used, with no SPE needed
- Good chromatographic peak-to-peak separation was achieved with an HPLC run time of 15 min (Figure 2)
- Excellent sensitivity was achieved with limit of quantification (LOQ) values at sub-ng/L levels, as shown in Figure 1
- The average accuracy (%) for PFAS standards in both solvent and spiked seawater samples was within acceptable criteria (70%–130%), and the area %CV <15% against an external calibration curve
- An external calibration curve in solvent and a standard addition workflow were easily implemented using SCIEX OS software to further confirm the concentration of PFAS compounds detected in un-spiked seawater samples

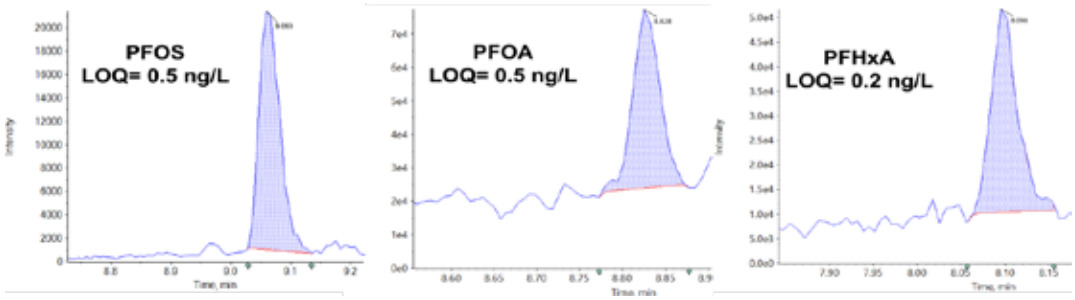

Figure 1. Extracted ion chromatograms (XICs) for PFAS compounds reported to be abundant in surface and subsurface seawater at their respective LOQs.[2] LOQ levels of 0.5 ng/L were achieved for PFOS and PFOA, and an LOQ level of 0.2 ng/L was achieved for PFHxA. This figure demonstrates the sensitivity and low-level quantification achieved on the SCIEX 7500 system. LOQ levels were determined by average accuracy (±30%), area %CV (<10%) and r^2 (>0.99).

MKT-26377-A

内容提要

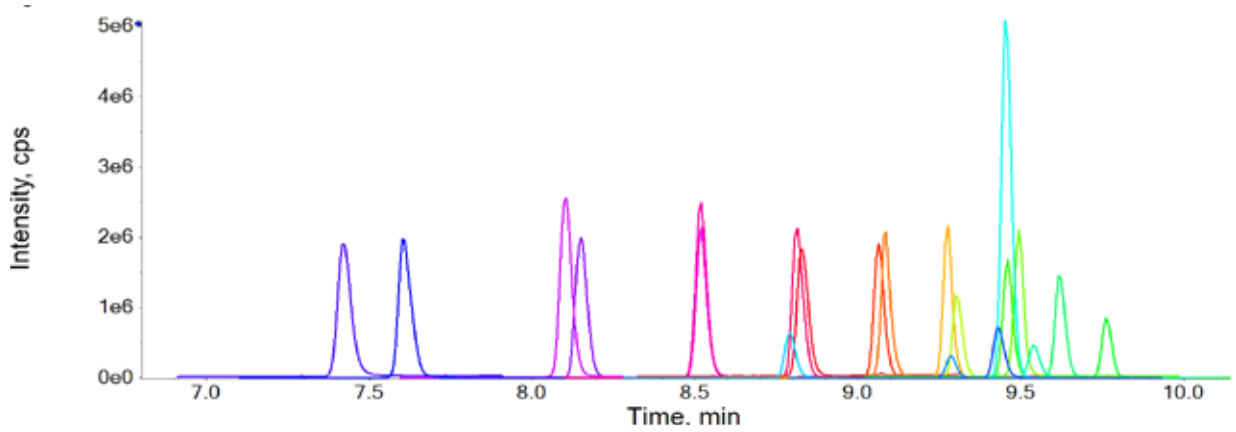

Figure 2. XICs of all PFAS compounds analyzed at 50 ng/L. Good chromatographic peak-to-peak separation was achieved.

Methods

Standard preparation: Mixed standards were prepared in a mixture of LC-MS water at a ratio of 2.5 mL LC-MS water to 2 mL 50:50 (v/v) acetonitrile/methanol + 0.22% formic acid.

Sample preparation: 2.5 mL of filtered seawater samples (collected from the Irish sea and filtered once with a 0.2 µm, 25 mm diameter Phenomenex regenerated cellulose (RC) syringe filter PN: AF0-8459) were added to 2 mL 50:50 (v/v) acetonitrile/methanol + 0.22% formic acid solution prior to analysis.

Chromatography: Chromatographic separation was performed using a Phenomenex Luna Omega PS C18, 100 Å, 100 mm x 2.1 mm, 3 µm (PN: 00D-4758-AN) column and a Phenomenex Gemini C18, 110 Å, 100 mm x 2.0 mm, 3 µm (PN: 00D-4439-B0) delay column. The injection volume was 50 µL and a flow rate of 0.4 mL/min was used. Mobile phase A was 20mM ammonium acetate in water and mobile phase B was methanol. Gradient conditions are shown in Table 1.

Table 1. Chromatographic gradient program.

Time (min)	% A conc	% B conc
0.0	*90*	*10*
1.5	*90*	*10*
8.0	*1.0*	*99*
12.0	*1.0*	*99*
12.5	*90*	*10*
15.0	*90*	*10*

Mass spectrometry: The analysis was performed using a SCIEX 7500 system operated with electrospray ionization in negative ion mode. The optimized source and gas parameters were similar to those in a previously published SCIEX technical note.[6]

Data processing: Processing was performed using SCIEX OS software 3.0. The peak-to-peak algorithm was used for signal-to-noise (S/N) determination.

Ultra-trace level sensitivity of PFAS standards in solvent

Table 2 highlights the LOQ values that were achieved for the PFAS compounds tested with this method in solvent (n=3). The criteria for LOQ determination were based on an average accuracy (%) of 70%–130% and an area %CV of <15%. The lowest current limit for PFAS compounds set by the European Parliament and Council of the European Union for drinking water is 100 ng/L. Table 2 illustrates the excellent levels of sensitivity achieved using this method.

In addition, the linearity of each PFAS compound was evaluated (Table 2) with all r^2 values >0.99 using a 1/x weighting. Figure 3 shows the calibration curve for PFOS and the respective r^2 value.

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Table 2. LOQ for each PFAS compound analyzed in diluent. Three commonly reported PFAS compounds in seawater are highlighted in bold (PFOS, PFHxA and PFOA). The peak-to-peak S/N algorithm was used, and S/N is included to show each peak is quantifiable with S/N >10.

Compound name	Chemical formula	LOQ (ng/L)	Peak-to-peak S/N
PFOS	***C8HF17O3S***	***0.50***	***17.0***
PFHxA	***C6HF11O2***	***0.20***	***23.3***
PFOA	***C8HF15O2***	***0.50***	***15.6***
PFNA	*C9HF17O2*	*0.20*	*15.7*
6:2 FTS	*C8H5F13SO3*	*0.50*	*35.1*
8:2 FTS	*C10H5F17SO3*	*0.50*	*25.6*
N-EtFOSSA	*C12H8F17NO4S*	*0.20*	*33.4*
N-MeFOSSA	*C11H6F17NO4S*	*0.50*	*15.5*
FOSA	*C8H2F17NO2S*	*0.50*	*41.0*
PFUdS	*C11HF23O3S*	*0.20*	*18.8*
PFDS	*C10HF21O3S*	*0.20*	*20.1*
PFBS	*C4HF9O3S*	*0.10*	*41.1*
PFPeS	*C5HF11O3S*	*0.10*	*35.1*
PFPeA	*C5HF9O2*	*0.20*	*21.2*
PFHpA	*C7HF13O2*	*0.20*	*25.8*
PFHxS	*C6HF13O3S*	*0.20*	*14.3*
PFHpS	*C7HF15O3S*	*0.20*	*17.3*
PFDA	*C10HF19O2*	*0.50*	*26.2*
PFNS	*C9HF19O3S*	*0.20*	*20.1*
PFDoS	*C12HF25O3S*	*0.50*	*18.8*
PFUdA	*C11HF21O2*	*0.50*	*14.8*

Precision and accuracy in 10 ng/L standard

Precision and accuracy were further assessed through multiple injections of a 10 ng/L standard (n=6). Table 3 shows that each PFAS compound was within the acceptable criteria with an average accuracy (%) of ±30% and an area %CV of <15%. Specifically, for the 3 PFAS commonly detected in seawater (PFOS, PFHxA, PFOA) the average accuracy ranged from 93.4-99.9% and the area %CV ranged from 2.8-7.5%.

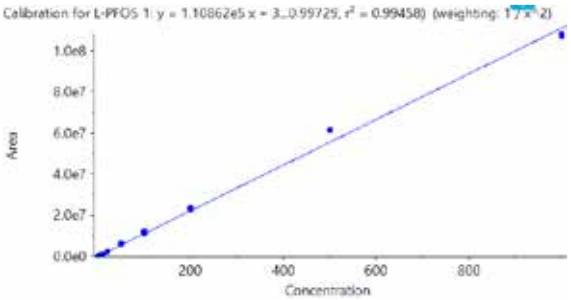

Figure 3. Calibration curve for PFOS. The linear range is 0.2–1,000 ng/L and r^2 >0.99 (weighting 1/x).

Table 3. The area %CV and average accuracy (%) across six standard injections at 10 ng/L. For each PFAS compound in diluent analyzed, the area %CV values are ≤15% and average accuracy (%) values are 70%–130%. Three commonly reported PFAS compounds in seawater are highlighted in bold (PFOS, PFHxA and PFOA).

Compound name	Area %CV	Average accuracy (%)
PFOS	*6.7*	*99.9*
PFHxA	*2.8*	*95.3*
PFOA	*7.5*	*93.4*
PFNA	*14*	*98.5*
6:2 FTS	*4.8*	*108*
8:2 FTS	*6.2*	*98.5*
N-EtFOSSA	*4.4*	*107.8*
N-MeFOSSA	*6.7*	*101.4*
FOSA	*7.6*	*125*
PFUdS	*6.0*	*98.3*
PFDS	*5.2*	*97.6*
PFBS	*4.2*	*101*
PFPeS	*7.2*	*96.9*
PFPeA	*2.3*	*104*
PFHpA	*3.8*	*101*
PFHxS	*4.6*	*103*
PFHpS	*5.0*	*106*
PFDA	*13*	*100*
PFNS	*3.2*	*89.5*
PFDoS	*6.3*	*90.9*
PFUdA	*12.2*	*91.6*

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Spiked seawater samples

Un-spiked and spiked seawater samples (10 ng/L) were injected to assess accuracy. Table 4 provides a summary of the calculated concentration of PFAS compounds in un-spiked seawater injected once (correction has been applied based on the average area of detected PFAS compounds in un-spiked seawater samples) when compared to the external standard calibration curve. Figure 6 highlights the XICs of three PFAS compounds, including the blank, un-spiked and spiked seawater samples.

Table 4. The concentration (conc) of PFAS compounds in the un-spiked sample (ng/L) and the accuracy of PFAS compounds analyzed with a 10 ng/L spike. As shown in the table, accuracy (%) values for a 10 ng/L spiked sample were 86.4%–124.8%.

Compound name	Un-spiked conc (ng/L)	Spiked conc: 10 ng/L	Accuracy (%): 10 ng/L spiked
PFOS	*<LOQ*	*10.4*	*99.6*
PFHxA	*0.54*	*10.1*	*103.9*
PFOA	*1.91*	*12.5*	*100.5*
PFNA	*<LOQ*	*9.23*	*88.5*
6:2 FTS	*<LOQ*	*10.8*	*108*
8:2 FTS	*ND*	*10.1*	*106*
N-EtFOSSA	*ND*	*10.2*	*102*
N-MeFOSSA	*ND*	*12.1*	*112*
FOSA	*ND*	*12.5*	*125*
PFUdS	*ND*	*8.64*	*86.4*
PFDS	*ND*	*9.22*	*92.2*
PFBS	*0.61*	*11.6*	*109*
PFPeS	*ND*	*10.1*	*101*
PFPeA	*0.58*	*11.2*	*102*
PFHpA	*0.54*	*10.9*	*93.4*
PFHxS	*<LOQ*	*10.9*	*109*
PFHpS	*ND*	*11.5*	*115*
PFDA	*ND*	*11.0*	*110*
PFNS	*ND*	*9.53*	*95.3*
PFUdA	*ND*	*8.67*	*86.7*

**** ND = not detected, <LOQ = below the limit of quantification***
**** Blank correction has been applied based on the average area of detected PFAS compounds in un-spiked seawater samples for average accuracy (%) for compounds spiked at 10 ng/L***

The average accuracy and precision were assessed for four of the most commonly reported PFAS compounds spiked at 10 ng/L in order to gain an average accuracy and %CV of area. Table 5 shows the calculated concentration of PFOS, PFHxA, PFOA and perfluorononanoic acid (PFNA) compounds in un-spiked seawater when compared to the external standard calibration curve, area %CV and average accuracy (%) for three injections at 10 ng/L.

Average accuracy was within acceptable criteria (70%–130%) and area %CV was ≤4.3% for spiked samples. From Table 4 and 5, we see comparable levels of PFOS, PFOA, PFHxA and PFNA in un-spiked seawater, which demonstrates the sensitivity, robustness, and reproducibility of this method.

Table 5. The average concentration (conc) of PFOS, PFHxA, PFOA and PFNA in the un-spiked sample (ng/L), area %CV (n=3) and average accuracy (n=3) analyzed at a 10 ng/L spike. As shown in the table, all area %CV is ≤4.26 and average accuracy (%) is 116%–127%.

Compound name	Mean un-spiked conc (ng/L)	Mean spiked conc: 10 ng/L	Mean spiked conc (corrected): 10 ng/L	%CV of area: 10 ng/L spiked	Mean accuracy (%): 10 ng/L spiked
PFOS	*<LOQ*	*12.7*	*12.4*	*3.2*	*123*
PFHxA	*0.85*	*13.4*	*12.7*	*3.9*	*127*
PFOA	*2.08*	*14.1*	*11.6*	*4.3*	*116*
PFNA	*<LOQ*	*12.6*	*12.1*	*0.94*	*121*

****<LOQ= less than the limit of quantification***
**** Correction has been applied based on the average area of detected PFAS compounds in un-spiked seawater samples for average accuracy (%) and concentration for compounds spiked at 10 ng/L***

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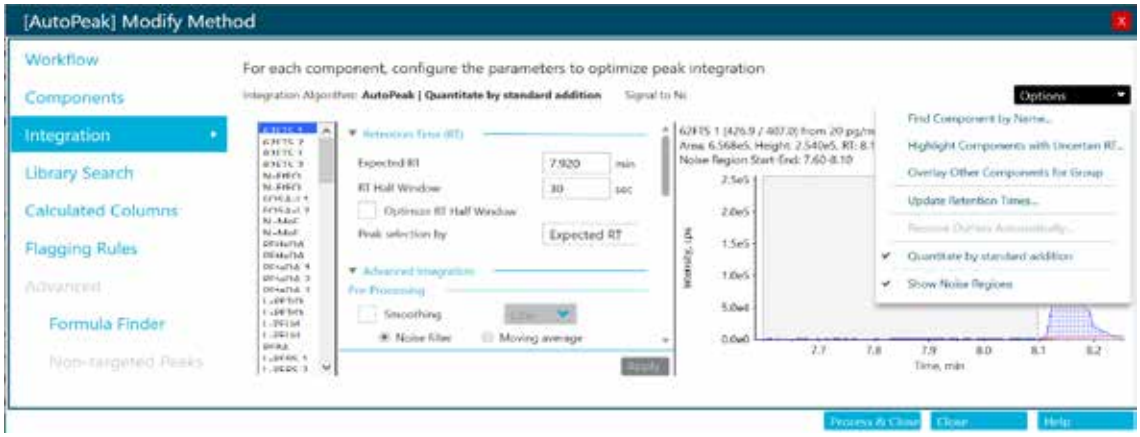

Figure 5. The "Quantitate by standard addition" function can be easily implemented in the process method. The function can be enabled under Integration > Options.

Standard addition in SCIEX OS improves quantification confidence

Standard addition is an analytical technique that improves quantification accuracy in samples with high matrix effects, for example complex environmental samples with high backgrounds. Standard addition is beneficial when surrogate standards are not readily available.[7] In this study, an external standard calibration curve in solvent and a standard addition workflow was assessed to determine the suitability of an external standard calibration curve for seawater. See Figure 4, which highlights the standard addition calibration curve for PFNA.

Table 6 compares PFAS compounds detected in un-spiked seawater on two different SCIEX 7500 systems when using the standard addition function in SCIEX OS software. The concentration of PFAS compounds detected in un-spiked seawater is comparable on both instruments when using standard addition. The average concentration of PFAS compounds in un-spiked seawater (Table 6) is also comparable to the concentrations calculated against the external standard calibration curve shown in Table 4, highlighting the robustness of this analytical method. Therefore, for this application, standard addition is viable when quantifying PFAS in the low ng/L range in seawater.

Table 6. The concentration of PFAS compounds detected in un-spiked seawater using the standard addition function in SCIEX OS software. The data below were acquired on two different SCIEX 7500 systems.

Compound name	Instrument 1: Average concentration of un-spiked standard addition (ng/L)	Instrument 2: Average concentration of un-spiked standard addition (ng/L)
PFOS	*<LOQ*	*<LOQ*
PFHxA	*0.74*	*0.94*
PFOA	*2.34*	*2.06*
PFNA	*<LOQ*	*<LOQ*
6:2 FTS	*0.35*	*0.46*
PFHpA	*1.10*	*1.22*
PFHxS	*<LOQ*	*<LOQ*

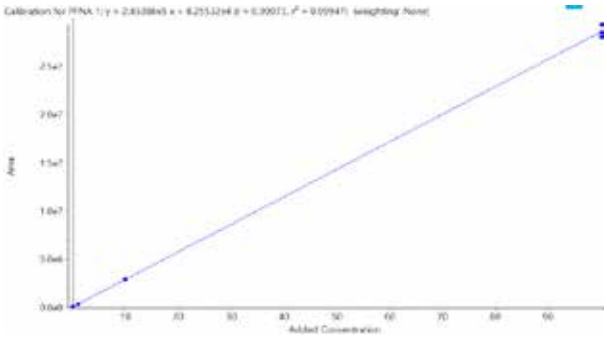

Figure 4. Standard addition calibration curve in seawater for PFNA. The embedded standard addition function in SCIEX OS software was used. Spiked concentrations were 1, 10 and 100 ng/L. An r^2 value of 0.99973 was obtained

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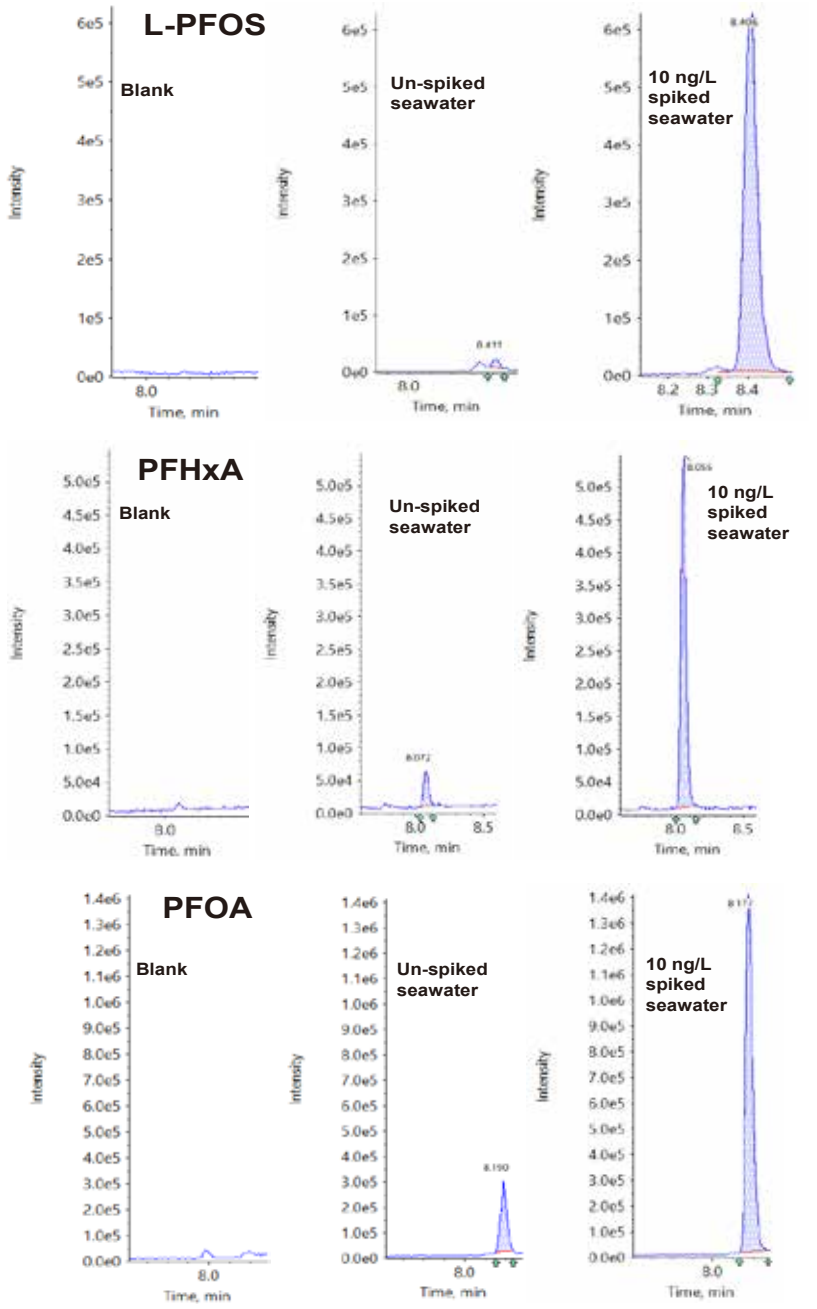

Figure 6. XICs of PFOS, PFHxA and PFOA. From left to right: blank, un-spiked seawater sample and 10 ng/L spiked seawater sample.

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Conclusions

- It is possible to achieve high-level sensitivity when analyzing PFAS compounds in the low ng/L range using the SCIEX 7500 system
- For PFAS standards in solvent, the area %CV was <15% and average accuracy (%) was 89.5%–125.5%, which were all within acceptable criteria (<15% for %CV and 70%–130% for average accuracy)
- For PFAS compounds (PFOS, PFHxA, PFOA and PFNA), excellent precision, accuracy and linearity were achieved in seawater samples, confirming the robustness and reproducibility of the method
- Both an external standard calibration curve and a standard addition workflow can be used for quantification of PFAS in seawater samples
- All PFAS compounds detected in the un-spiked seawater samples were at low ng/L levels

References

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3. PFAS in the upstream oil and gas industry. March 2021
4. Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption. Official Journal, L 435, 1-62.
5. Confident quantification of per- and polyfluoroalkyl substances in water intended for human consumption. SCIEX technical note, RUO-MKT-02-13414-A.
6. An ultra-high sensitivity analysis of PFAS compounds in multiple water sources. SCIEX technical note, RUO-MKT-02-15059-A
7. Standard addition processing simplified with SCIEX OS software. SCIEX technical note, RUO-MKT-07-7660-B.

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Non-targeted acquisition with suspect screening for novel PFAS identification in river water and sediment samples

Using the X500R QTOF system to analyze and characterize emerging PFAS

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[1]SCIEX (Framingham, MA); [2]UNC-Wilmington (Wilmington, NC)

This technical note demonstrates the identification of novel PFAS compounds in river, aquifer water and sediment using non-targeted acquisition with suspect screening. Analysis was performed using the X500R QTOF system with SWATH acquisition and processed using SCIEX OS software. PFAS identification was performed using MS/MS library matching and diagnostic fragment confirmation. Samples were collected near Wilmington, North Carolina, an area known to have been impacted by perfluoroalkyl ether carboxylic acids (PFECAs) and perfluoroalkyl ether sulfonic acids (PFESAs).

Targeted analysis methods, such as the EPA drinking water methods, cover only a small fraction of the approximately 5000 per- and polyfluoroalkyl substances (PFAS). Non-targeted analysis using liquid chromatography and high-resolution mass spectrometry increases the analytical coverage of PFAS present and overcomes the challenges of characterizing emerging PFAS. Quadrupole time-of-flight (QTOF) instruments, such as the X500R QTOF system, provide information on the precursor mass and the MS/MS fragmentation spectra, which is critical for elucidating unknown PFAS (Figure 1).

Key features of the X500R QTOF system and SCIEX OS software

- SWATH DIA acquisition on the X500R QTOF system acquires MS/MS spectra on all detectable compounds, providing comprehensive fragmentation fingerprints for identification
- Experimentally determined high-resolution and accurate mass of the detected peak and the FormulaFinder feature generates candidate empirical formulae
- Analytics module in SCIEX OS software links the candidate formula to possible structures with the extensive ChemSpider database
- MS/MS spectra data is used to evaluate candidate structures by matching in silico fragmentation pattern prediction of candidate structures

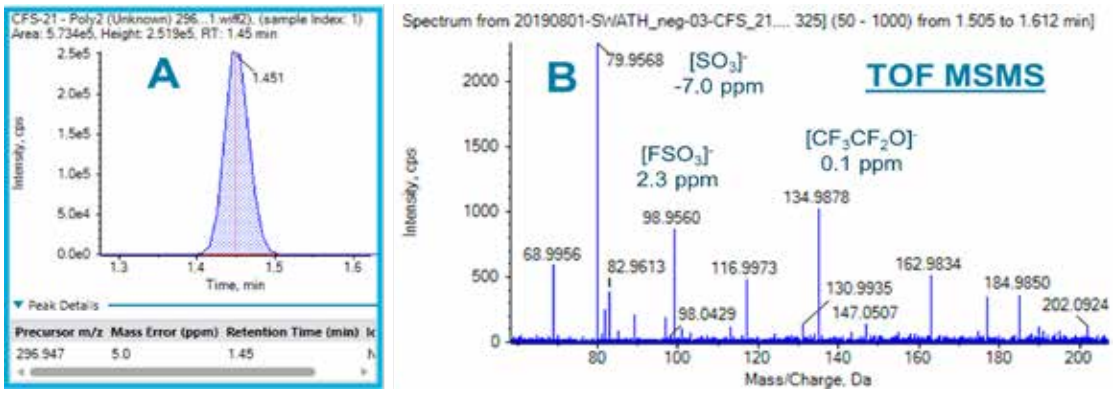

Figure 1. Identification of NVHOS ($C_4F_8H_2O_4S$) in Cape Fear River sediment using suspect screening. Left panel (A) shows TOF MS XIC with good mass error (5 ppm). Right panel (B) shows TOF MS MS spectrum with matches to theoretical fragments. Identification confidence level 2b.

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Methods

Sample preparation: River and aquifer water and sediment samples were collected from the Cape Fear River in Wilmington, NC, using methanol-cleaned HDPE bottles and bags. Sample preparation followed published methods.[1] River water samples were filtered and extracted using Oasis WAX Plus SPE cartridges, and the final eluate was reduced to 1 mL. Sediment samples were dried at 40° C and extracted with 20:80 MilliQ water: methanol three times. Extracts were cleaned with ENVI-CARB SPE cartridges, and the eluant was reduced to 0.5 mL The final vial composition was 100% methanol.

Chromatography: The SCIEX ExionLC system was modified to replace the fluoropolymer tubing with PEEK and included a delay column to separate PFAS contamination from the LC system. Analytes were separated using a Phenomenex Luna Omega C18 PS column (100 Å, 50 x 2.1 mm, 1.6 µm particle size) using gradient conditions. The mobile phases were water ("A") and methanol ("B"), both modified with 10 mM ammonium acetate with a flow rate of 0.4 mL/min. The column oven was 40°C, and the injection volume was 10 µL. Initial conditions were 10% "B", immediately ramped to 55%, and then ramped to 70% B over 2.9 min. The gradient was then ramped to 99% B over 0.1 min, held for 0.9 min, and returned to initial conditions for a total run time of 6.5 min.

Mass spectrometry: Mass spectrometry analysis was performed using the X500R QTOF system with electrospray ionization (ESI) in negative mode. Samples were analyzed using SWATH acquisition, a data-independent acquisition technique that collects MS/MS spectra for all precursor compounds. TOFMS scans were performed from 100-1000 Da with DP = -40V, CE = -5V and accumulation time of 0.05 sec. Variable SWATH windows were chosen so that window widths were narrowest in regions with the highest precursor density. TOFMSMS scans ranged from 50 to 1000 Da with DP= -40V, CE= -35V and CES = 30V and accumulation time of 0.05 sec. The total scan time was 0.60 sec, resulting in approximately 10-12 data points across the chromatographic peak.

Data processing: The data was processed in suspect and non-targeted screening workflows with the Analytics module in SCIEX OS software 2.1.

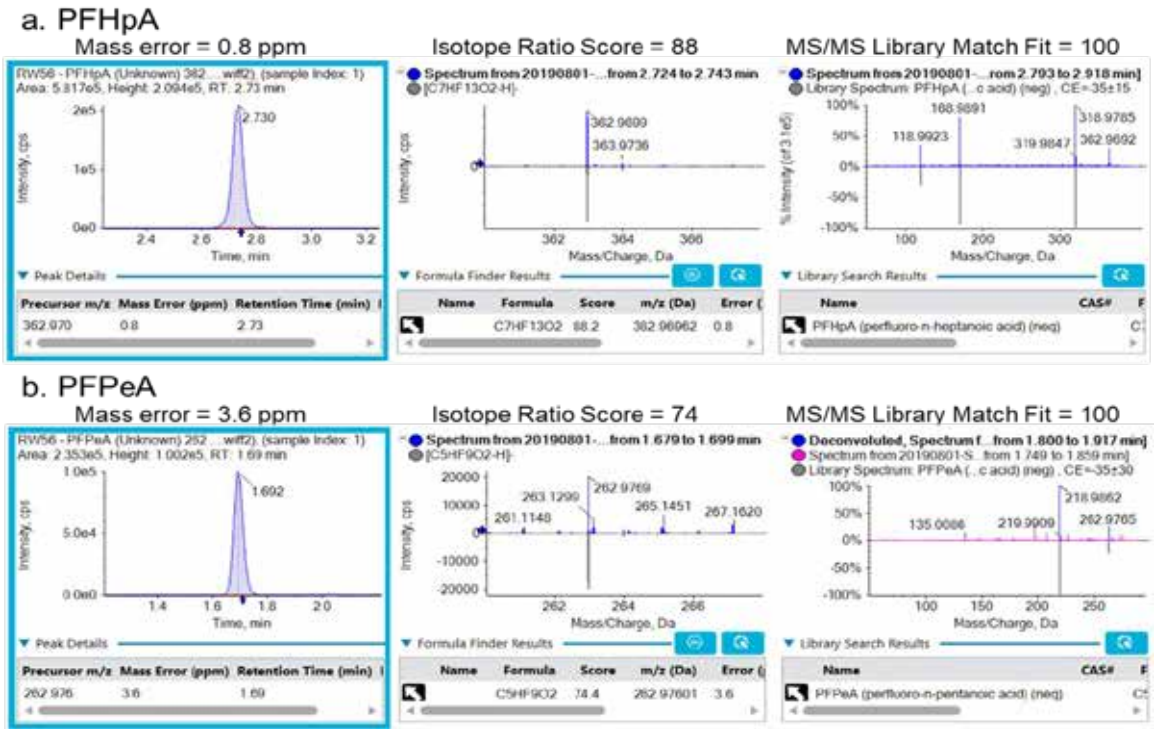

Figure 2. Legacy PFAS identified in Cape Fear River surface water through suspect screening. PFHpA (top panel) and PFPeA (bottom panel) confirmed by precursor mass error, TOF MS isotope pattern and MS/MS library match. Identification confidence level 1a.

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Suspect screening with MS/MS library searching for legacy PFAS

Suspect screening workflows monitor a list of target compounds, utilizing either the chemical formula or exact mass to generate the extracted ion chromatogram (XIC). The compound identification is confirmed using the exact precursor mass error (accuracy <5 ppm) and isotope ratio score. Further, the MS/MS spectrum is compared to a library database for additional confidence. The SCIEX HR-MS/MS Fluorochemical library 2.0 is a verified library containing MS/MS spectra for ~250 PFAS compounds covering negative, positive and zwitterionic compound classes. For example, this approach was used to confirm the detection of two short-chain PFAS in the river water sample, PFPeA and PFHpA (Figure 2). Both PFAS compounds showed good precursor mass error and isotope pattern match and strong MS/MS library match (library "fit" score = 100 for both compounds). The deconvolution algorithm helps to produce a cleaner fragementation spectrum by removing MS/MS ions from interfering, co-eluting precursors that are not associated with the compound of interest. For example, the SCIEX OS software deconvolution algorithm resulted in a cleaner MS/MS spectrum for PFPeA and improved library matching (Figure 2b).

Novel PFAS suspect screening using MS/MS from published data for confirmation

Suspect screening lists may also be generated from novel PFAS compounds in the literature[2]. The suspect compounds may not be in the Fluorochemical library and can be confirmed based on their mass error, isotope ratio and MS/MS spectrum. In this situation, the predominant MS/MS fragments are manually compared between the experimental and literature-published MS/MS spectrum.

For example, figure 1 shows the identification of NVHOS ($C_4F_8H_2O_4S$) in a sediment sample. The SCIEX OS software shows a good mass error (5 ppm). Further, the major MS/MS fragment ions of $[SO_3]^-$, $[FSO_3]^{-\cdot}$ and $[CF_3CF_2O]^-$ were present, which is consistent with spectra reported in the literature[1, 2]. Based on recent reporting criteria[3], the identification confidence was level 2b. Figure 3 shows another example of using this approach, the positive detection of the PFESA Byproduct 2 compound in a sediment sample. The software showed excellent mass error (-0.3 ppm) and isotope ratio score (84.4), and the major experimental MS/MS fragment ions matched those from chemical standard[1]. In addition, PFESA byproducts identified are shown in Table 1.

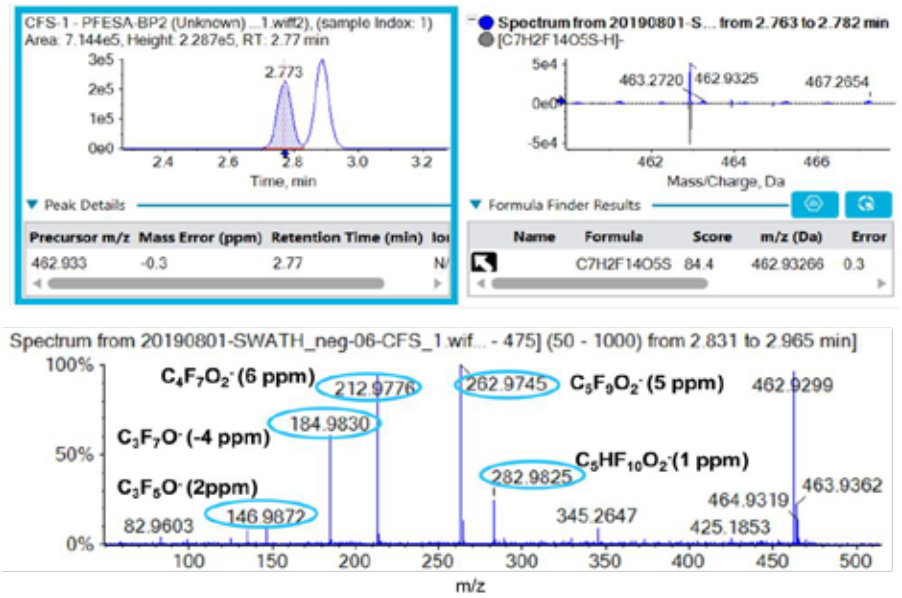

Figure 3. Identification of PFESA Byproduct 2 in a sediment sample from the Cape Fear River based on mass error, isotope matching and MS/MS spectrum. The top left panel shows the TOF MS XIC, the two constitutional isomers were chromatographically separated. The top right panel shows the experimental TOF MS spectrum (blue) and theoretical TOF MS spectrum (grey, mirrored). The bottom panel shows the TOF MSMS spectrum; circled fragments were confirmed against the published MS/MS spectrum from a chemical standard[1]. Identification confidence level 2b

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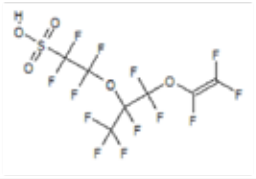
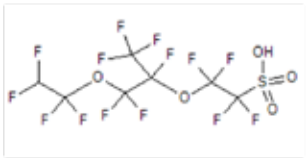
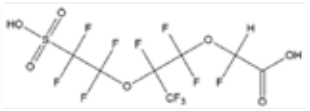
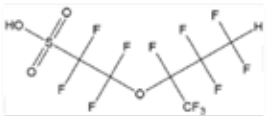
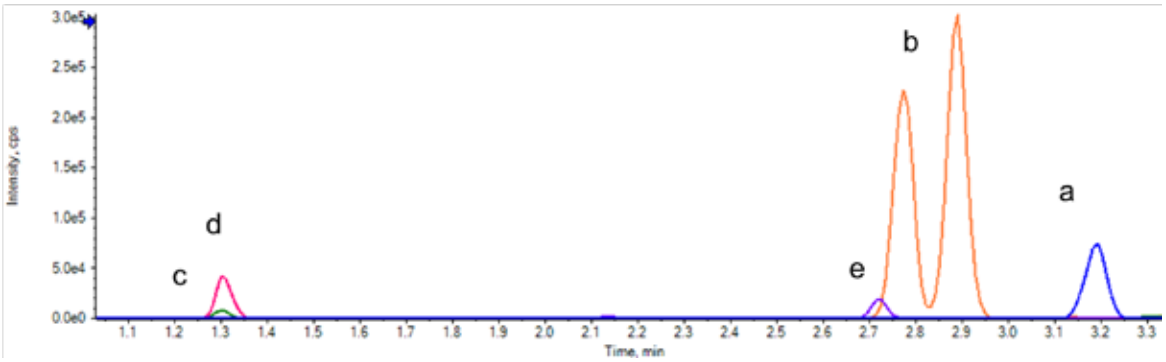
Table 1. Identification of PFESA Byproducts 1-5 from a Cape Fear River sediment samples using suspect screening with confirmation by TOF MS mass error and diagnostic MS/MS fragment ions.

Compound name	Formula	TOF MS mass error (ppm)	Structure	Peak
PFESA-BP1	$C_7HF_{13}O_5S$	0.7		a
PFESA-BP2	$C_7H_2F_{14}O_5S$	-0.3		b
PFESA-BP3	$C_7H_2F_{12}O_6S$	0.1		c
PFESA-BP4	$C_7H_3F_{11}O_7S$	0.2		d
PFESA-BP5	$C_6H_2F_{12}O_4S$	-0.3		e



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Non-target data filtering using Kendrick mass defects

Non-target screening workflows return ion characteristics from the features identified by the peak-finding algorithm, including molecular mass, fragment spectra and isotope composition. Highly fluorinated molecules, such as PFAS, are typically characterized by a negative mass defect, defined as the difference between the exact and nominal mass of the compound. To screen for and readily visualize potential novel PFAS, the non-target data was processed using these mass defects[2] and Kendrick mass defects (KMD) with different repeating units (-CF_2-, -CF_2O-, -C_2F_4O-)[4].

Figure 4 shows that the KMD plots visually identified 9 homologous groups of highly fluorinated compounds in the compiled Cape Fear River samples (i.e., river and aquifer water, sediment samples). Features that fall along the same horizontal line are related to each other and differ only by the number of -CF_2 (top panel) or CF_2O-(bottom panel) units. For example, the perfluorinated sulfonic acid group (e.g., PFOS, PFHxS) was observed along the line corresponding to KMD (-CF_2) of 0.038 units, and the perfluorinated carboxylic acids (e.g., PFOA) were observed along KMD (-CF_2) of 0.007 units.

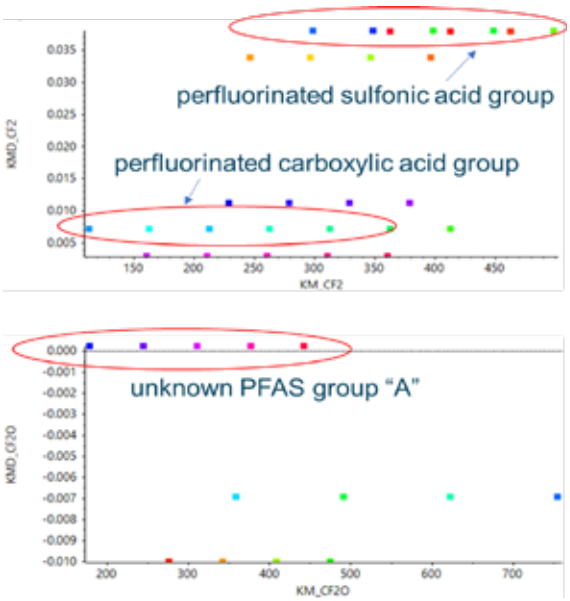

Figure 4. KMD plots generated from all river and aquifer, and sediment samples from the Cape Fear River. Nine groups of homologs were identified in the KMD plot with repeating units of -CF2- (top) and -CF2O- (bottom).

In addition, KMD plots were used to prioritize the resulted peaks for further identification using Formula Finder and ChemSpider features and expansion of suspect list. For example, the KMD (-CF_2O) plot showed a homologous series of unknown compounds with KMD (-CF_2O) of approximately 0.00 units.

Characterization of emerging PFAS using Formula Finder and ChemSpider in SCIEX OS software

The group of unknown compounds prioritized from the KMD plots in Figure 4 was further characterized using Formula Finder and ChemSpider in SCIEX OS software. These SCIEX OS software modules help characterize emerging PFAS without MS/MS library matches or literature-reported spectra. Specifically, Formula Finder generates candidate empirical formulae based on the TOF MS accurate mass and a user-defined set of potential elements. Then, the generated candidate formulae are matched to structures from ChemSpider database. Within ChemSpider, the experimental MS/MS spectra were compared to the predicted fragmentation pattern of the candidate structures.

Figure 5 shows the characterization workflow for one feature identified in the KMD plot unknown group, m/z 244.9693, in the aquifer water. Formula Finder identified a potential formula of $C_4HF_7O_4$, and ChemSpider matched the diagnostic m/z 84.9907 fragment (-CF_3O), ultimately identifying PFO_2HxA.

To further screen unknown PFAS in this homologous series, a suspect list was built that contained differing -CF_2O repeating units based on PFO_2HxA. Ultimately, four additional perfluoropolyether were added to the suspect list and confirmed using their diagnostic ions and mass accuracy (Table 2).

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Conclusions

- Multiple PFAS classes were detected using non-target analysis in surface and aquifer water, and sediments from the Cape Fear River basin
- Legacy PFAS, such as the perfluorinated carboxylic acids, were identified using suspected screening with fragment matching from the SCIEX Fluorochemical MS/MS library
- Novel PFAS identified by suspect screening and matching diagnostic MS/MS fragments
- Kendrick Mass Defect plots are used to detect homologous series of novel PFAS with identification through SCIEX OS software Formula Finder and ChemSpider for structural elucidation

References

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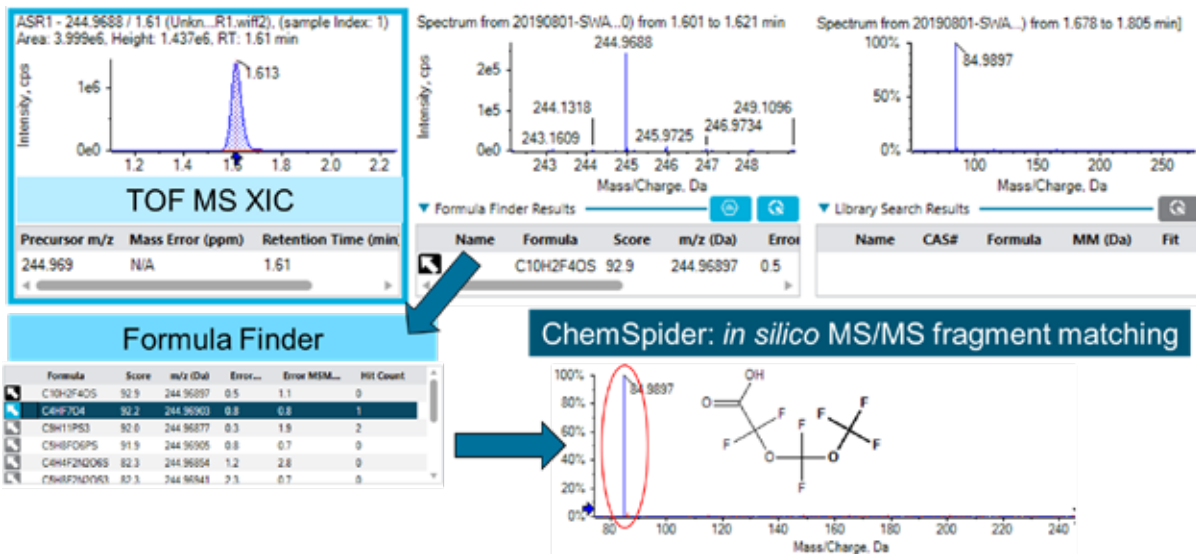

Figure 5. Non-target analysis workflow using Formula Finder and ChemSpider in Analytics module of SCIEX OS software for the identification of PFO_2HxA in Cape Fear River aquifer water. Formula Finder generated the candidate empirical formulae. Then, a candidate formula was matched to structures from ChemSpider database. Empirical MS/MS spectrum were matched to fragmentation pattern prediction of candidate structures. Identification confidence level 3c.

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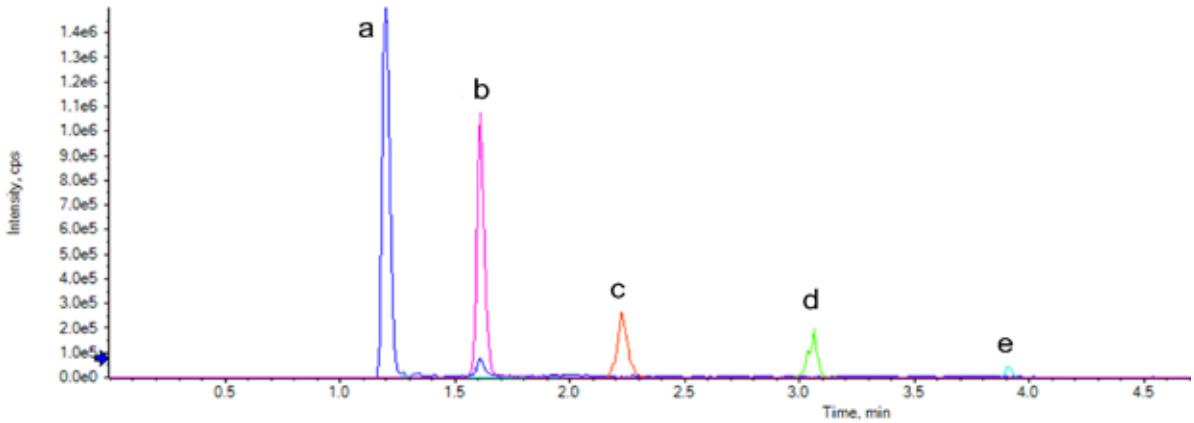
Table 2. Perfluoropolyether compounds identified in the Cape Fear River aquifer water samples by suspect screening.

Compound name	Structure	TOF MS mass error (ppm)	MS/MS fragment mass errors (Da)	Peak
PFMOAA		*2.1*	*<0.01*	*a*
PFO_2HxA		*0.8*	*<0.001*	*b*
PFO_3OA		*0.6*	*<0.01*	*c*
PFO_4DA		*0.5*	*<0.07*	*d*
PFO_5DoDA		*0.8*	*<0.001*	*e*



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内容提要

Use of electron activated dissociation (EAD) to elucidate PFAS structures

Karl Oetjen[1], Craig M. Butt[2], Megumi Shimizu[2], Diana Tran[1]
[1] SCIEX, Golden, CO, USA; [2] SCIEX, Framingham, MA, USA

Introduction

Poly- and perfluoroalkyl substances (PFAS) are well-known environmental contaminants and are widely detected in humans and wildlife, water, soil and air.[1,2] PFAS are primarily used for their stain repellency properties as well as their surfactant characteristics, such as in aqueous film-forming foams (AFFF) to combat petroleum fires. Even though there are an estimated 5,000 unique PFAS manufactured, most monitoring efforts are focused on only 20-30 compounds. Non-targeted data acquisition using high resolution accurate mass spectrometry is beneficial for elucidating unknown compound structures, such as PFAS in complex samples. However, candidate structure assignment depends crucially on the collection of high-quality MS/MS spectral data. Traditional fragmentation methods using collision-induced dissociation (CID) can be too aggressive to form diagnostic MS/MS spectra (Figure 1). Alternatively, electron activated dissociation (EAD) has shown potential as a form of fragmentation to produce more robust spectra.[3] This study evaluated the use of EAD fragmentation qualitative PFAS structure elucidation and compared the results to those produced with MS/MS spectra achieved using traditional CID generated data.

Key features of the ZenoTOF 7600 system for structural elucidation

- The ZenoTOF 7600 system collects high resolution spectral data using multiple types of fragmentation
- Electron activated dissociation (EAD) is a “softer” fragmentation strategy compared to the commonly applied collision-induced dissociation (CID)
- The capacity to select different fragmentation types allows the user to collect the greatest number of unique MS/MS fragments, which can be used for structural elucidation
- User-adjustable parameters such as kinetic energy settings allow for further refinement and optimization of the acquisition method to achieve the best MS/MS data
- Utilizing the EAD fragmentation strategy was observed to be advantageous in analyzing AFFF for PFAS, as the softer fragmentation strategy produces a greater number of unique fragments from PFAS species

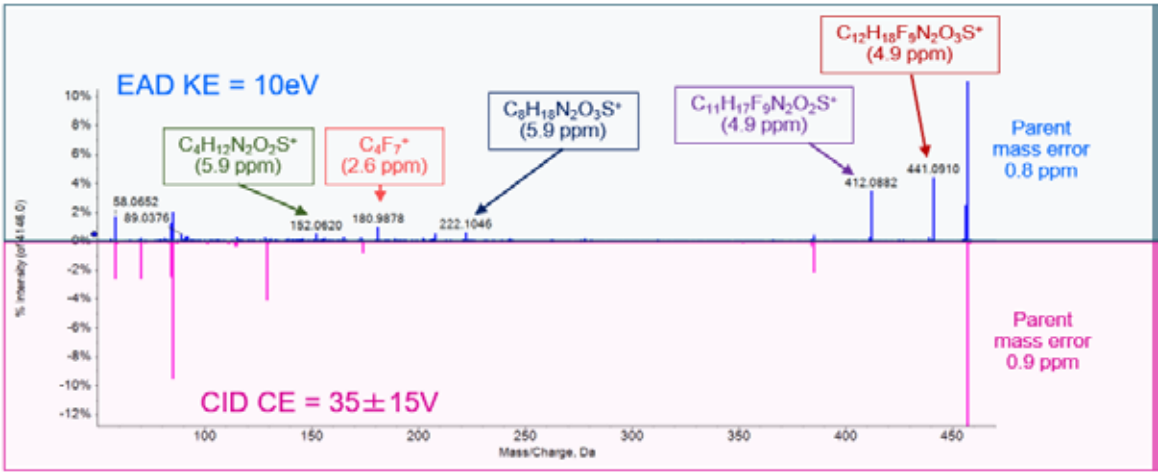

Figure 1. Fragmentation spectra generated using EAD fragmentation in an AFFF mixture. EAD spectral data (top spectrum) showed the generation of several unique fragments compared to CID fragmentation (bottom spectrum).

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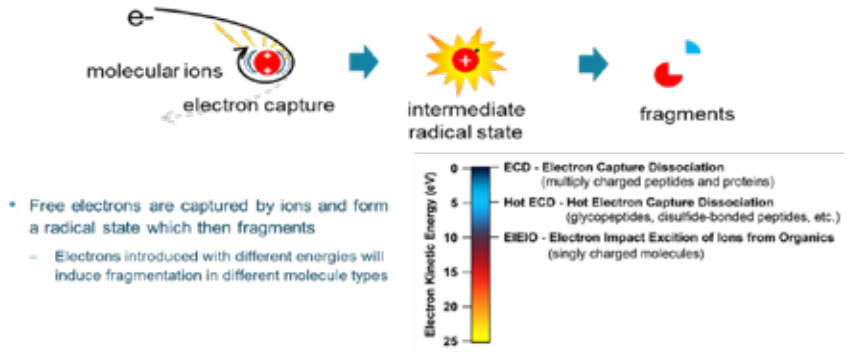

Figure 2. Mechanism of EAD fragmentation. Note that different kinetic energy settings produce fragmentation for different types of molecules.

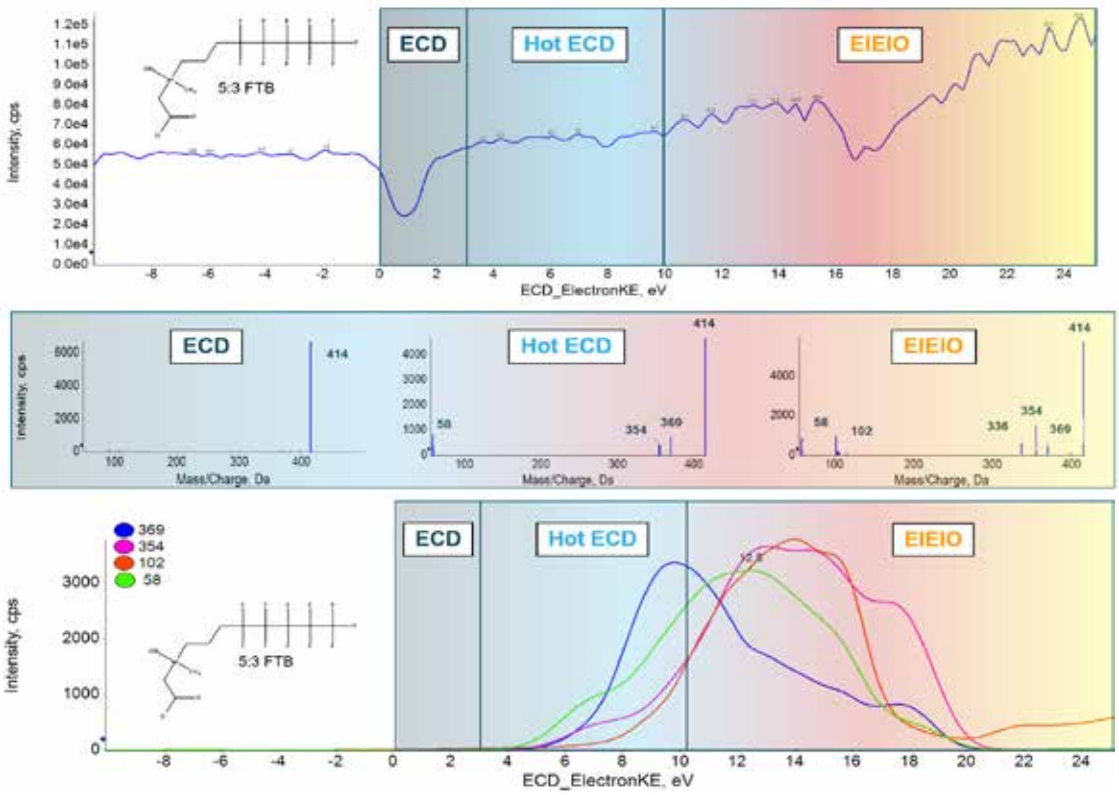

Figure 3. Kinetic energy ramping from -10 to 25 V using EAD fragmentation mode for the 5:3 FTB. Increased fragments were generated in the "hot ECD" (3 to 10 V) and "EIEIO" (10-25 V) regions.

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Methods

Standard solutions of 50 PFAS compounds including 5:3 fluorotelomer betaine (5:3 FTB), 5:1:2 FTB, AmPr-FHxSA, TAmPR-FHxSA and 6:2 FTSA-PrB were purchased from Wellington Laboratories (Guelph, ON). The standards were infused on the ZenoTOF 7600 system using both CID and EAD fragmentation modes. Figure 2 shows a brief visualization of the mechanism behind EAD fragmentation, including designation of relevant kinetic energy zones.[3] In separate EAD experiments, the kinetic energy (KE) was ramped from -10 to 25 V and the electron beam current ramped from 0 to 8000 V. Further, 10, 35, and 100 ms reaction times were tested. Finally, an AFFF mixture was injected on a reverse-phase LC column and subject to gradient conditions to compare EAD and CID fragmentation in a real-world PFAS AFFF sample. Data processing and evaluation were performed in the SCIEX OS software.

Results

Kinetic energy (KE) ramping

Initial EAD KE ramping experiments were performed using the 5:3 FTB. Results showed that low KE values (< 3 V) were insufficient to cause precursor compound fragmentation (Figure 3). However, fragmentation was observed as the KE increased into the "hot ECD" and "EIEIO" regions (Figures 2,3). Specifically, fragments *m/z* 369, *m/z* 354, *m/z* 102 and *m/z* 58 were detected as the KE values increased to greater than 5 V. All fragments showed maximum intensity in the EIEIO region, except for the *m/z* 369 fragment.

Comparing CID vs EAD fragmentation

To further explore the potential benefits of EAD fragmentation, the 5:1:2 fluorotelomer betaine was infused using both CID and EAD fragmentation. The MS/MS spectra generated from CID fragmentation showed only formation of the *m/z* 58.0651 Da fragment ($C_3H_8N^+$) under the 3 voltage ranges of collision energy (CE) tested; 10-20 V, 30-40 V and 50-60 V (Figure 4). In contrast, the MS/MS spectra generated from EAD fragmentation showed many more fragments produced in the 3 KE ranges, particularly at KE=16 V (Figure 5). EAD showed the generation of several unique fragments as compared to CID fragmentation.

Using EAD fragmentation to identify PFAS in an AFFF mixture

The AFFF mixture that was separated using liquid chromatography with gradient conditions showed the presence of the perfluorobutane sulfonamido propyl dimethyl quaternary amine propanoate when using both EAD and CID fragmentation. However, the EAD fragmentation spectrum showed additional, numerous unique fragments (Figure 5) that were not observed during CID fragmentation (Figure 1). Therefore, EAD fragmentation may act as an additional, orthogonal source of confirmation for the identification of unknown PFAS compounds.

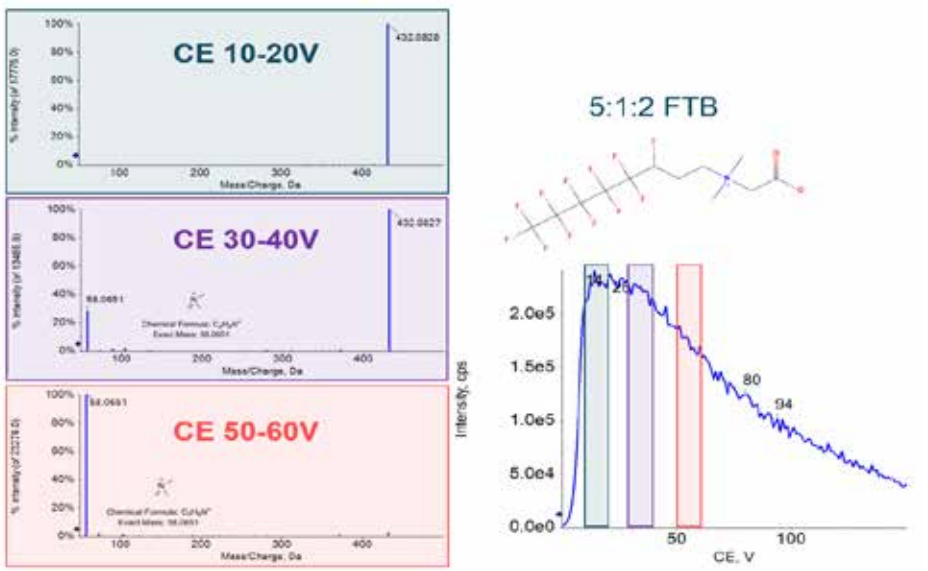

Figure 4. Left panels show fragmentation spectra generated using CID fragmentation of the 5:1:2 fluorotelomer betaine. Spectra are separated by the three CE ramps from 10-20V (top), 30-40V (center) and 50-60V (bottom). The only fragment observed during CID was the $C_3H_8N^+$ fragment at m/z 58.0651.

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Conclusions

In general, the MS/MS spectra collected using EAD generated more fragments which could be beneficial for confirming compound identity during nontarget analysis. During KE ramping, it was observed that different energy ranges produced different fragmentation patterns. Ramping the KE to “hot ECD” and EIEIO values showed unique fragments as compared to lower KE values. This study ultimately showed that the EAD fragmentation may provide additional or orthogonal spectral information for the identification of nontargeted PFAS structures.

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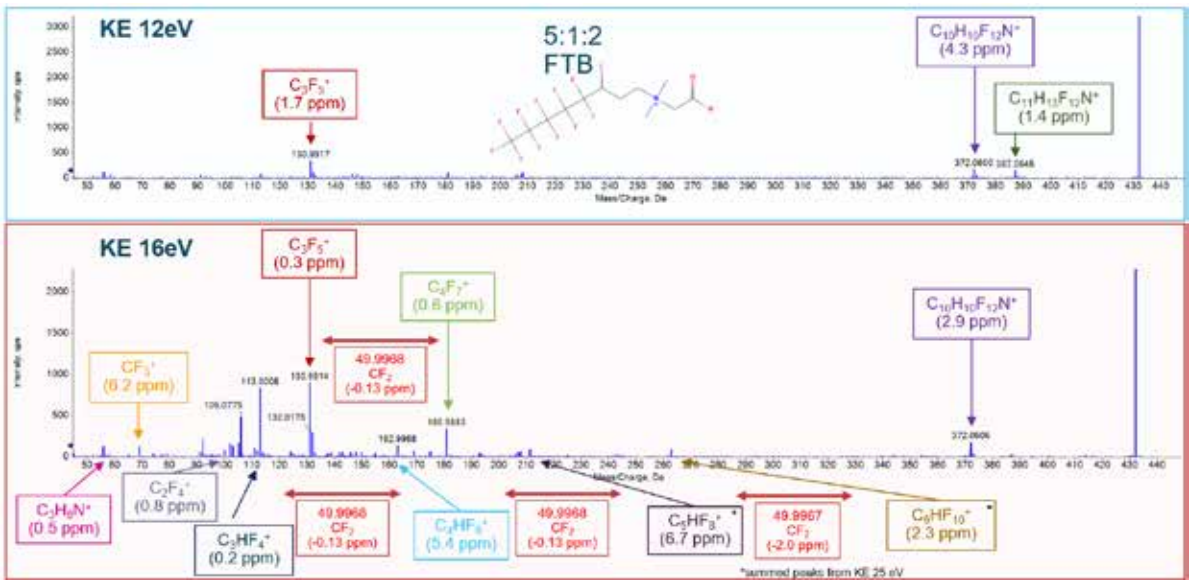

Figure 5. Fragmentation spectra generated using EAD fragmentation of the 5:1:2 fluorotelomer betaine at KE values of 12 eV (top) and 16 eV (bottom). The KE 12 eV spectrum showed the formation of 3 fragments while the KE 16 eV spectrum showed the formation of 16 unique fragments.

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内容提要

Non-targeted characterization of organic phosphate flame retardants (OPFRs) in aviation hydraulic fluid

Non-targeted acquisition with suspect screening using the X500B QTOF system

Matthew Standland[1], Craig Butt[1], and Pengguang Yu[2]
[1]SCIEX, USA; [2]PALL, USA

Optimized sample preparation and instrumental methods are presented to improve the detection and identification of unknown compounds in an aviation hydraulic fluid, ultimately improving its characterization. Specifically, extraction, chromatography, ionization, and acquisition parameters were developed using the SCIEX X500B QTOF system. The fast scan speed of the X500B resulted in high quality MS/MS spectra which improved compound identification confidence through MS/MS library matching.

Characterizing the chemical profile of industrial fluids is challenging due to their complexity. Non-targeted acquisition methods using time-of-flight mass spectrometers (QTOFs) are powerful techniques for unknown compound identification when combined with software such as SCIEX OS.

Aviation hydraulic systems provide the safe and effective mechanical operation of jet planes. Traditional mineral oil-based fluids have low flash points and have been responsible for some airplane fires[1]. As a result, aviation hydraulic fluids often contain additives, such as organic phosphate flame retardants (OPFRs)[1]. While OPFRs are beneficial in lowering aviation hydraulic fluid flammability, they are widely detected in the environment, such as in surface waters that contain low- to mid-level µg/mL concentrations of OPFRs, as reported by the CDC[2]. OPFRs have been linked to neurotoxicity, thyroid/endocrine regulation effects, and potential carcinogenicity[3] and are therefore a concern for human exposure.

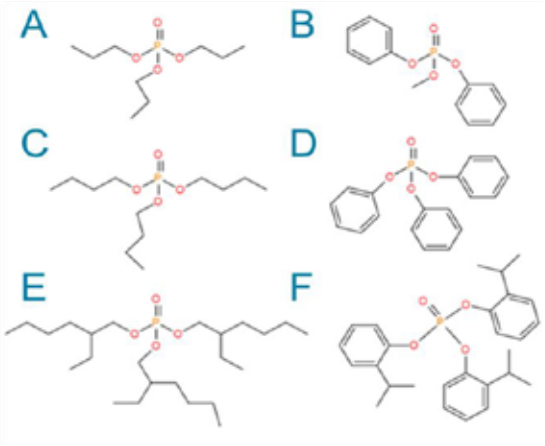

Figure 1. Representative OPFR compounds. A = tripropyl phosphate, B = diphenyl methyl phosphate, C = tributyl phosphate, D = triphenyl phosphate, E = tris (2-ethylhexyl) phosphate, F = isopropyl phenyl phosphate. OPFRs have broad structural variation about their phosphate/phosphite group. Aliphatic groups with or without branching, and phenyl groups with or without further attachment were found extensively in this survey.

Key features of hydraulic fluid analysis using the X500B QTOF system

- Simple acetone and methanol extraction scheme
- Easy transition between ESI and APCI probes for increased ionization coverage, depending on analyte properties
- Use of representative samples allows for rapid screening of unique compounds
- MS/MS spectral matching allows for high-confidence discovery using TOF MS/MS data
- SCIEX OS software component list used in conjunction with flagging rules allows for high-confidence identification of targets in TOF MS data

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Methods

Sample preparation: A 10 µL sample of aviation hydraulic fluid was mixed with 990 µL of acetone and vortexed. A 500 µL aliquot of this extract was then combined with 500 µL of methanol and vortexed again. The supernatant was filtered through a 0.2 µm nylon filter. A representative blank sample was generated by mixing 500 µL of acetone with 500 µL of methanol and then filtered with a 0.2 µm nylon filter.

Chromatography: Chromatography was optimized to reduce precursor concurrency. A Phenomenex Kinetex C8 column was used (2.6 µm, 50 x 2.1 mm) for both APCI and ESI experiments. Optimized APCI LC experiments used a 15 min gradient that ramped mobile phase A (1:1, methanol/water with 1% formic acid) to mobile phase B (80:20, methanol/isopropanol with 1% formic acid) with 1.0 mL/min flow rate and 4 µL injection. Optimized ESI LC experiments used a 20 min gradient that ramped mobile phase A (1:1, methanol/water with 0.1% formic acid and 5mM ammonium formate) to mobile phase B (1:1, methanol/isopropanol with 0.1% formic acid and 5mM ammonium formate) with 0.5 mL/min flow rate and 4 µL injection.

Mass spectrometry: APCI and ESI experimental conditions were optimized to achieve the highest total precursor output. For APCI experiments, the optimal conditions were GS1= 50, CUR = 40, TEM = 400 °C and nebulizer current = 3 µA. For ESI experiments, the optimal conditions were GS1= 50, GS2 = 40, CUR = 40, TEM = 400 °C and ISV = 2250 V.

In both ESI and APCI experiments, a data-dependent acquisition (DDA) method was run to fragment the 10 most abundant candidate ions in the TOF MS scan. Dynamic background subtraction was used, and only the first 2 unique spectra in a 10-second window were used for fragmentation.

Data processing: Samples were initially investigated using non-targeted screening in SCIEX OS software and potential matches were compared against the NIST MS/MS library (v1.0.1). Flagging rules filtered library matches with fit scores between 80% and 100%. The non-targeted screening results showed the detection of several OPFR compounds in the hydraulic fluid sample. Therefore, a comprehensive components list was built for suspect screening based on OPFRs previously reported in the literature. Figure 2 shows examples for 2 of the OPFRs found by library searching.

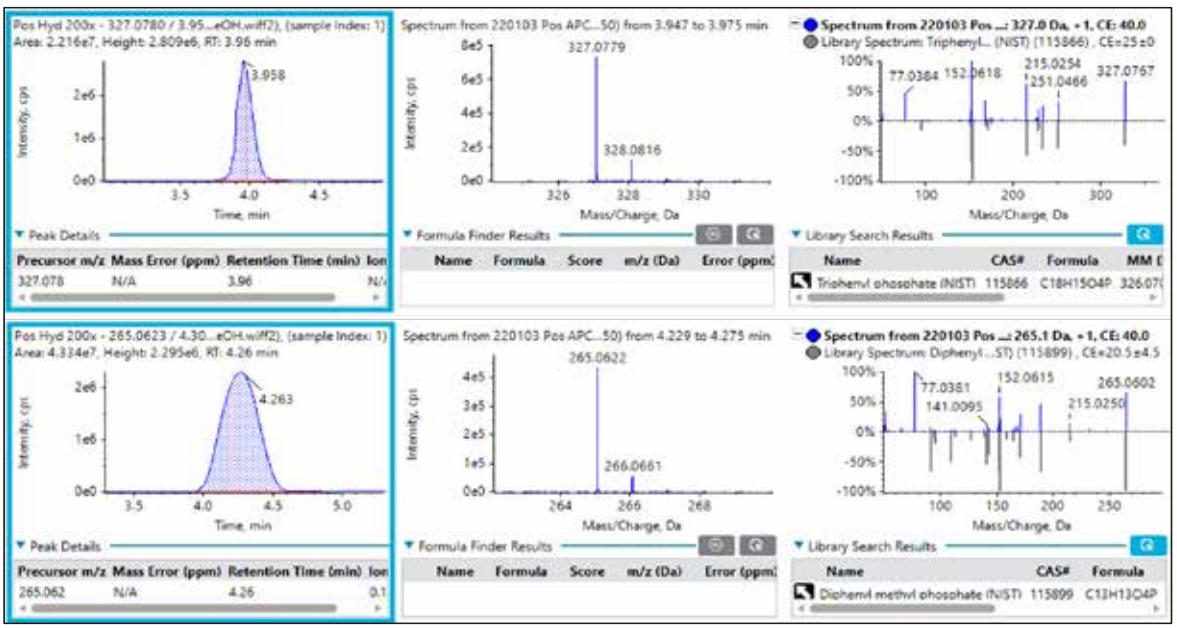

Figure 2. High-confidence library identification of OPFRs. Triphenyl phosphate (top) and diphenyl methyl phosphate (bottom) were detected in the hydraulic fluid with greater than 90% fit criteria against the NIST library MS/MS spectra.

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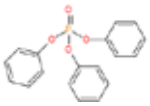
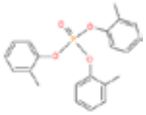
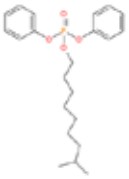
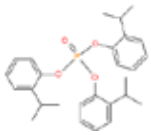
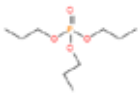
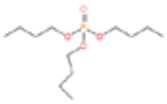
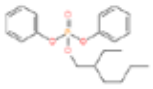
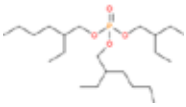
Table 1. OPFR compounds detected in the hydraulic fluid sample using the component list.

Compound	Structure	Formula	Mass error (APCI, ESI)/ppm	Area APCI	Area ESI
Triphenyl phosphate		$C_{18}H_{15}O_4P$	*-0.5*	*2.2e7*	*3.9e7*
Tricresyl phosphate		$C_{21}H_{21}O_4P$	*1.0*	*9.5e5*	*2.0e6*
Isodecyl diphenyl phosphate		$C_{22}H_{31}O_4P$	*0.9*	*3.0e6*	*1.5e7*
Isopropyl phenyl phosphate		$C_{27}H_{33}O_4P$	*0.9*	*4.1e5*	*1.1e6*
Tripropyl phosphate		$C_9H_{21}O_4P$	*0.6*	*1.9e6*	*Nd*
Trimethyl phosphate		$C_3H_9O_4P$	*-1.0*	*3.3e6*	*Nd*
Tributyl phosphate		$C_{12}H_{27}O_4P$	*-0.8*	*5.7e8*	*4.6e8*
2-ethylhexyl diphenyl phosphate		$C_{20}H_{27}O_4P$	*0.5*	*5.5e4*	*2.5e6*
Tris (2-ethylhexyl) phosphate		$C_{24}H_{51}O_4P$	*1.1*	*1.3e5*	*7.9e5*

Most compounds were found in ESI and APCI experiments. APCI mode performed better for smaller aliphatic OPFRs, whereas ESI mode performed better for highly branched and/or longer chain OPFR compounds

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Results

The initial objective was to produce the highest number of unique features by optimizing the LC and MS parameters. 431 features were identified using ESI mode, while 581 features were discovered using APCI mode.

Of the 25 compounds surveyed via the OPFR suspect screening list, several were found in either ESI datasets, APCI datasets or both. Figure 3 shows representative chromatograms and MS/MS spectra acquired from these experiments, highlighting the low mass error and high-quality isotopic distribution. Table 1 displays findings and relative peak areas for each compound detected in ESI and APCI experiments. Many of these compounds were not initially discovered during the library search, however, they can be added easily to an existing library using SCIEX OS software.

This technical note demonstrates how industrial chemicals, such as aviation hydraulic fluids, can be characterized using the X500B QTOF system coupled with SCIEX OS software. OPFR chemicals were discovered during non-targeted screening and were then comprehensively investigated during suspect screening.

Conclusions

- OPFR compounds were discovered in different abundances, depending on the optimized APCI or ESI conditions implemented
- X500B collected high-quality MS/MS spectra resulting in increased compound identification confidence through MS/MS spectral library matching
- SCIEX OS software makes the discovery and consolidation of important metrics in complex datasets a seamless process

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3. Trowbridge J. et al. (2022) Organophosphate and Organohalogen Flame-Retardant Exposure and Thyroid Hormone Disruption in a Cross-Sectional Study of Female Firefighters and Office Workers from San Francisco. Environ. Sci. Technol. **56 (1)**, 440-450.

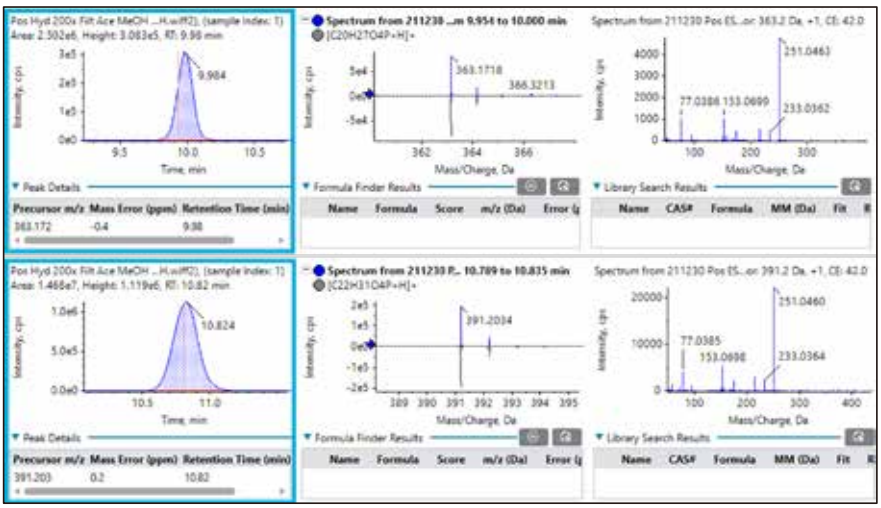


Figure 3. OPFR compounds detected via the components list. 2-ethylhexyl diphenyl phosphate (top) and isodecyl diphenyl phosphate (bottom) were detected among several other compounds listed in Table 1. Both compounds exhibited excellent mass accuracy and TOF MS isotopic distribution.

RUO-MKT-02-14640-A

内容提要

环境水中176种PPCPs及农药污染物的筛查和定量方法

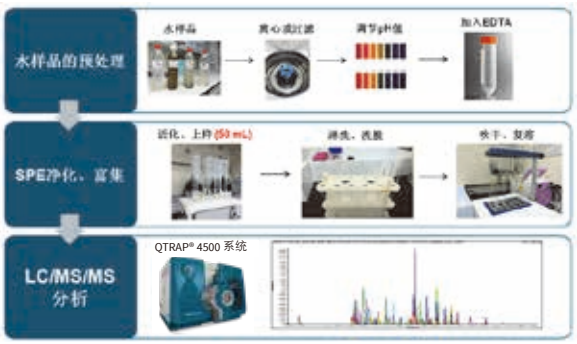
基于SCIEX液相色谱三重四极杆/线性离子阱复合质谱 QTRAP® 4500系统

贾彦波，朱怀恩，赵贵平，刘华芬

SCIEX 中国

近年来，环境水中的新型微量有机污染物——药物和个人护理品（Pharmaceuticals and Personal Care Products, PPCPs）已引起公众和学术界的广泛关注，检测分析环境水中PPCPs的挑战在于存在水体中的PPCPs浓度非常低（ng/L, ppt级别），且污染物种类来源广泛；本文介绍了用SCIEX QTRAP® 4500系统建立了一套环境水中176种PPCPs的筛查和定量分析方法，并获得了非常好的结果。

环境水样品的分析流程：



1. 176种有机污染物 (PPCPs和农药) 的种类

抗生素和激素：β-内酰胺类 (18), 喹诺酮类 (16), 磺胺类 (18), 大环内酯类 (11), 四环素类 (13), 激素类 (14)；

其它药品和护理品：精神类 (15), 糖尿病类 (6), β-Blocker (4), 哮喘、镇咳 (5), 兴奋剂 (4), 心血管类 (12), 广谱抗菌 (7), 解热镇痛 (6), 胃酸和抗凝剂 (3)；

农药：氨基甲酸酯类 (16), 苯氧羧酸类 (8)。

2. 样品前处理——简单、快速

水样品量需50 mL，极大地降低了SPE的上样时间；采用3 mL，60 mg的小体积SPE柱，最后洗脱体积仅3 mL，大大降低了氮气吹干洗脱液的时间，整个样品处理过程仅需2个小时左右。

3. LC-MS/MS方法分组少，分析时间短 --- 高通量

质谱采用电喷雾（ESI）正负离子化、MRM采集方式，同一液相色谱方法，LC-MS/MS分析时间为13.5 min。

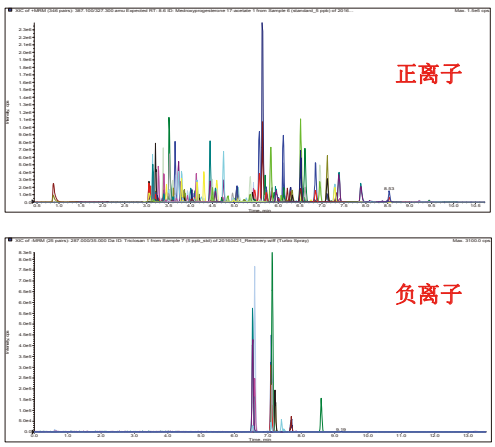


图1. 176种浓度为5 ng/mL的PPCPs标准品色谱图。

4. LC-MS/MS方法灵敏度高，筛查和定量结果可靠

1) 与美国EPA 16941方法相比，本方法具有更高的灵敏度。

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	EPA 1694[1] IPR* Criteria			本方法**		
	LLOQ (ng/L)	Recovery (%)	RSD (%)	LLOQ (ng/L)	Recovery (%)	RSD (%)
N-乙酰对氨基酚	200	55-108	30	1	100.5	4.7
无水四环素	50	8-127	30	1	68.3	12.3
咖啡因	50	55-111	30	1	80.1	4.8
1,7-二甲基黄嘌呤	500	55-124	30	1	97.8	9.0
头孢噻肟	20	9-168	36	5	124.1	10.7
沙拉沙星	200	18-180	32	5	97.4	7.5
青霉素V	20	6-180	30	5	92.8	8.6
三氯森	200	55-108	30	10	114.1	4.8
磺胺	50	6-170	71	10	94.7	5.3
氨苄青霉素	5	6-180	70	5	88.4	11.6
林可霉素	10	6-108	60	1	92.3	1.3
苯唑西林	10	6-180	30	5	99.6	1.0
罗红霉素	1	42-108	30	1	92.3	4.1
三甲氧苄胺嘧啶	5	55-114	30	1	114.6	4.7
脱氢硝苯地平	2	47-108	30	1	111.7	3.5
氟西汀	10	54-112	30	1	100.9	2.5
诺孕酯	10	39-108	30	1	92.6	2.9
杀鼠灵	5	55-108	30	1	108.4	3.1
甲地孕酮	NA***	NA	NA	1	119.9	1.4
雌二醇	NA	NA	NA	10	100.6	8.3
安宫黄体酮	NA	NA	NA	1	102.1	2.7
倍他洛尔	NA	NA	NA	1	105.3	4.5

*: IPR: Initial precision and recovery **：浓度50 ng/L，N = 3 ***：EPA1694不包括的化合物。

2) 可快速筛查出环境水样品中未知的有机污染物。

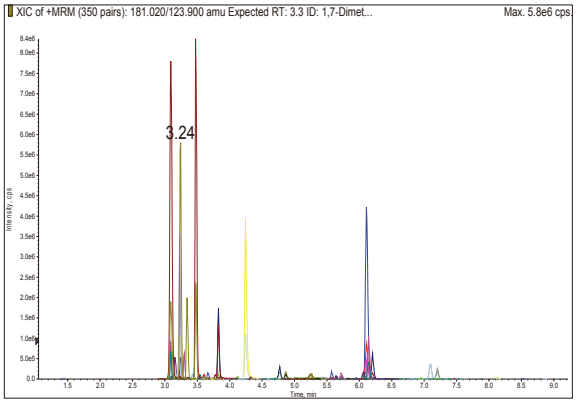

图2. 某城市污水处理厂入口处污水样品的色谱图。

表1. 某城市污水处理厂入口处污水的筛查结果。

大环内酯类 (7)	**噻诺酮类 (3)**	**兴奋剂、镇咳、哮喘 (7)**	**精神类疾病 (4)**
阿奇霉素 (叠氮红霉素)	磺胺甲基异恶唑 (新诺明)	咖啡因	多虑平
林可霉素 (洁霉素)	磺胺嘧啶 (磺胺哒嗪)	1,7-二甲基黄嘌呤	舒必利
罗红霉素	三甲氧苄胺嘧啶	可替宁	卡巴咪嗪 (卡马西平)
甲红霉素 (克拉霉素)	磺胺二甲(基)嘧啶	右美沙芬	奥沙西泮
克林霉素	磺胺吡啶	可待因	**日用生活抗菌 (4)**
红霉素	**β-内酰胺类 (4)**	二羟丙茶碱	甘宝素
脱水红霉素	头孢氨苄	沙丁胺醇	三氯卡巴 (三氯卡班)
四环素类 (4)	3-去乙酰基头孢噻肟	**高血压 (8)**	氟康唑
四环素	头孢拉定	厄贝沙坦	噻苯咪唑 (噻菌灵)
无水四环素	头孢噻肟	替米沙坦	**氨基甲酸酯类农药 (5)**
地霉素(土霉素)	**胃酸 (2)**	缬沙坦	灭多威
氯四环素	甲腈咪胺, 西咪替丁	洛沙坦	克百威 (呋喃丹)
解热镇痛 (4)	雷尼替丁(甲硝呋胍)	地尔硫卓	残杀威
N-乙酰对氨基酚	**糖尿病 (4)**	脱氢硝苯地平	异丙威
安替比林	格列齐特	阿替洛尔	仲丁威
氨基比林	格列本脲	索他洛尔	**抗过敏、晕车 (1)**
非那西丁	瑞格列奈	**激素类 (4)**	苯海拉明
局部麻醉 (1)	格列美脲	甲地孕酮	**抗凝剂、鼠药 (1)**
利多卡因		17a-雌二醇	华法令
		安宫黄体酮 (醋酸甲孕酮)	**心血管 (1)**
		可的松	西地那非

3) 准确定量环境水样品中有机污染物的浓度。

表2. 某城市污水处理厂入口处污水中环丙沙星的浓度为23.02 ng/L。

Sample Name	Sample Type	Component Name	Actual Concentration	Area	Calculated Concentration	Accuracy
5	Standard	Ciprofloxacin 1	5.00	1.62e4	5.14	102.73
10	Standard	Ciprofloxacin 1	10.00	2.59e4	9.39	93.93
25	Standard	Ciprofloxacin 1	25.00	6.62e4	26.77	107.06
100	Standard	Ciprofloxacin 1	100.00	2.26e5	95.65	95.65
250	Standard	Ciprofloxacin 1	250.00	5.86e5	250.07	100.03
500	Standard	Ciprofloxacin 1	500.00	1.17e6	502.58	100.60
Sample	Unknown	Ciprofloxacin 1	N/A	5.76e4	23.02	N/A

5. 该方法包括详细且完整的实验操作流程，从样品前处理，到LC-MS/MS方法，定量方法及结果报告模板，并经实验内与实验室间方法学验证，是真正“拿来即用”的LC-MS/MS方法，大大节省了方法开发的时间。

RUO-MKT-02-4429-ZH-A

内容提要

总结

本文建立了一套检测环境水中176种PPCPs和农药污染物的筛查和定量LC-MS/MS方法，覆盖有机污染物种类广，样品前处理快速、简单，LC-MS/MS方法具有分析时间短，通量高，检测灵敏度高等特点，可快速筛查和定量环境水样品中的未知有机污染物。该方法包括了详细的实验操作流程，大大节省了方法开发时间，是真正“拿来即用”的LC-MS/MS方法。

参考文献：

1. Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS.

RUO-MKT-02-4429-ZH-A

内容提要

QTRAP® 6500+系统直接进样法同时检测生活饮用水中57种抗生素

QTRAP® 6500+ system direct sampling method for simultaneous detection of 57 antibiotics in drinking water

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Key words: QTRAP® 6500+ system, antibiotics, drinking water, direct sampling

生活饮用水中抗生素检测难点

1. 抗生素种类繁多，性质又各不相同，同时检测可能存在一些问题，比如，四环素类化合物存在差向异构体；喹诺酮类化合物存在吸附现象等等。
2. 抗生素在环境水体中的含量很低（ng/L），需要浓缩。
3. 常规需要固相萃取法，缺点是难以兼顾种类性质各不相同的抗生素，且耗费时间较长。

QTRAP® 6500+系统直接进样法特点

1. QTRAP® 6500+系统灵敏度高，水样经过0.22 μm微孔滤膜过滤后可直接进样。
2. QTRAP® 6500+系统配备IonDrive™ Turbo V™离子源，抗基质干扰能力强，生活饮用水、地表水、河流域水等均可以实现滤膜过滤后直接进样。
3. QTRAP® 6500+系统配备IonDrive™ High Energy 检测器，可实现5 ms超快速正负离子切换且不损失灵敏度，一针进样即可完成57种抗生素的检测。

实验方法

色谱条件：

A相：水+0.1甲酸　　B相：乙腈+0.1甲酸

色谱柱：Proshell 120 EC-C18, 3×100 mm, 2.7 μm

流速：0.8 mL/min

大体积进样

质谱条件：（正负离子同时扫描）

离子源参数

Curtain gas (psi)：30

CAD gas：8

Ionspray voltage (V)：2500/-4500

Temperature(℃)：600

Ion source gas1 (psi)：45

Ion source gas2 (psi)：45

MRM离子对信息（共57种抗生素）见表1

标准曲线的制备

取50 mL水到50 mL离心管中，加入25 mg EDTA，再加入15 μL盐酸(36~38%)，制得水样的pH约为3，取该溶液逐级稀释获得标准曲线。

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内容提要

样品制备

取50 mL水样到50 mL离心管中，加入25 mg EDTA，再加入15 μL盐酸(36~38%)，制得水样的pH为3，样品经过滤膜过滤后，进样分析。

实验结果

1. 57种抗生素提取离子流色谱图展示：

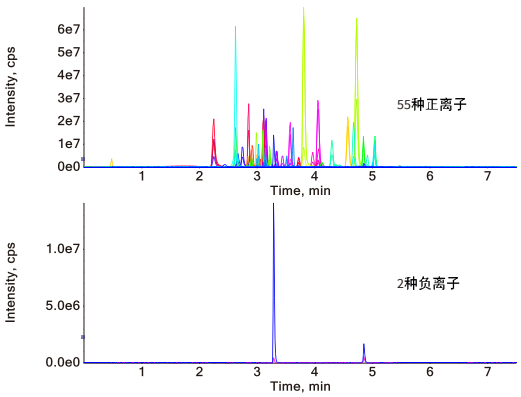

图1. 57种抗生素提取离子流色谱图

2. 标准曲线展示：采用大体积进样方式，57种抗生素的定量限均可达到ng/L水平。

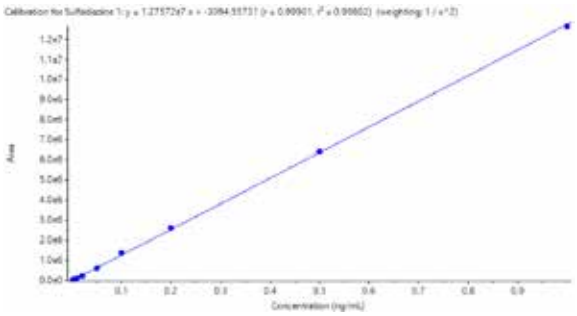

图2. 磺胺嘧啶标准曲线举例

3. 基质样品重现性考察：生活饮用水基质加标（0.05 μg/L），6针连续进样，57种抗生素峰面积的RSD值均在2%以内，如图3所示：

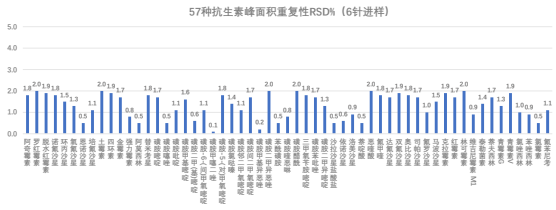

图3. 57种抗生素基质样品加标重现性统计

4. 基质干扰考察，相同浓度（0.05 μg/L）生活饮用水样品与纯溶剂样品进行对比，数据统计显示，57种抗生素基质抑制的百分比不超过13%，如图4所示：

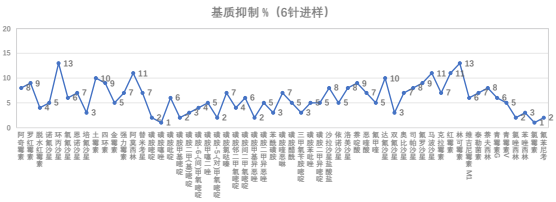

图4. 57种抗生素基质抑制统计

总结

1. 本文通过QTRAP® 6500+系统开发了一针进样分析生活饮用水中57种不同种类的抗生素的检测方法，包括大环内酯类、喹诺酮类、四环素类、氯霉素类、磺胺增效剂、磺胺类、β-内酰胺类，其中有55种为正离子，2种为负离子。QTRAP® 6500+系统配备IonDrive™ High Energy检测器，可以实现5 ms超快速的正负离子切换，并且不损失灵敏度。

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2. 本方法采用的是高流速且大体积进样的方式，结合QTRAP® 6500+系统强大的定量能力，57种抗生素的定量限均可达到ng/L水平，可满足生活饮用水中抗生素检测的灵敏度需求。

3. 抗生素种类繁多，且性质各不相同，前处理一般会采用多种固相萃取法相结合才能完全覆盖，操作复杂，一般耗时可达几小时，并且回收率难以保证，本方法采用直接滤膜（0.22 μm）过滤法，前处理操作简单，1 min以内即可完成。

4. QTRAP® 6500+系统配备IonDrive™ Turbo V™离子源，抗基质干扰能力强，为直接进样法提供了可能，生活饮用水、地表水、河流域水等均可以实现滤膜过滤后直接进样。

表1 MRM离子对信息列表（共57种抗生素）

编号	中文名称	扫描方式	Q1	Q3	DP	CE
1	阿奇霉素	正离子	749.6	591.5	110	31
			749.6	116.1	110	70
2	罗红霉素	正离子	837.6	679.5	80	30
			837.6	158.1	80	41
3	脱水红霉素	正离子	716.6	558.4	100	23
			716.6	540.3	100	27
4	诺氟沙星	正离子	320.1	276.1	80	26
			320.1	233.1	80	35
5	环丙沙星	正离子	332.1	288.1	80	25
			332.1	314	80	30
6	氧氟沙星	正离子	362.2	318.1	80	26
			362.2	261.1	80	38
7	恩诺沙星	正离子	360	316.1	80	25
			360	245.1	80	35
8	培氟沙星	正离子	334.1	316.1	80	27
			334.1	290.2	80	25
9	土霉素	正离子	461.2	426.2	80	27
			461.2	443.2	80	20
10	四环素	正离子	445.1	410	95	28
			445.1	427	95	19
11	金霉素	正离子	479.1	444	80	28
			479.1	462	80	24
12	强力霉素	正离子	445	428	95	25
			445	154	95	38
13	阿莫西林	正离子	366.2	113.9	60	26
			366.2	208	60	19
14	替米考星	正离子	435.3	695.2	90	23
			435.3	522.3	90	31
15	磺胺嘧啶	正离子	251.1	156	40	22
			251.1	92	40	38
16	磺胺噻唑	正离子	256	156	40	22
			256	108	40	32
17	磺胺吡啶	正离子	250.1	156.1	40	23
			250.1	108	40	32
18	磺胺甲基嘧啶	正离子	265.2	156.1	82	25
			265.2	172.1	82	25
19	磺胺二甲(基)嘧啶	正离子	279.11	186.1	60	23
			279.11	156	60	27
20	磺胺-6-(间)甲氧嘧啶	正离子	281.1	156	75	25
			281.1	126.1	75	30
21	磺胺甲噻二唑	正离子	271	156.1	65	21
			271	108	65	36
22	磺胺-5-(对)甲氧嘧啶	正离子	281.1	156.1	70	25
			281.1	108.1	70	35
23	磺胺氯哒嗪	正离子	285.1	156	65	22
			285.1	108.1	65	37
24	磺胺邻二甲氧嘧啶	正离子	311.11	156.1	70	30
			311.11	108.1	70	70

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表1 MRM离子对信息列表（共57种抗生素）（续）

编号	中文名称	扫描方式	Q1	Q3	DP	CE
25	磺胺间二甲氧嘧啶	正离子	311.1	156.1	70	28
			311.1	218	70	28
26	磺胺甲基异恶唑	正离子	254.1	156	65	22
			254.1	108	65	36
27	磺胺二甲异恶唑	正离子	268.1	156.1	82	22
			268.1	113.2	82	25
28	苯酰磺胺	正离子	277.1	156	60	19
			277.1	108	60	32
29	磺胺喹恶啉	正离子	301.1	156	80	24
			301.1	108	80	36
30	磺胺醋酰	正离子	215	156	52	17
			215	108	52	29
31	三甲氧苄胺嘧啶	正离子	291.1	230.1	95	33
			291.1	123.1	95	34
32	磺胺苯吡唑	正离子	315	156	90	27
			315	108	90	40
33	磺胺二甲异嘧啶	正离子	279.1	124.1	80	30
			279.1	186.1	80	23
34	沙拉沙星盐酸盐	正离子	386	342.3	80	25
			386	299	80	38
35	依诺沙星	正离子	321	303	80	24
			321	234	80	30
36	洛美沙星	正离子	352	265	80	33
			352	308.1	80	28
37	萘啶酸	正离子	233	215	68	18
			233	187	68	34
38	恶喹酸	正离子	262	244.1	70	26
			262	216.1	70	40
39	氟甲喹	正离子	262.1	244.1	77	23
			262.1	202.1	77	42
40	达氟沙星	正离子	358.1	340.1	77	30
			358.1	314.1	77	24
41	双氟沙星	正离子	400.1	356.1	80	28
			400.1	299.1	80	41
42	奥比沙星	正离子	396	352	80	24
			396	295.2	80	32
43	司帕沙星	正离子	393	349.2	80	30
			393	292	80	38
44	氟罗沙星	正离子	370	326.1	80	27
			370	269.2	80	35
45	马波沙星	正离子	363.1	320.1	80	23
			363.1	72	80	46
46	克拉霉素	正离子	748.5	590.4	40	29
			748.5	158.0	40	40
47	红霉素	正离子	734.5	576.4	30	26
			734.5	158.0	30	36
48	林可霉素	正离子	407.3	126.1	30	32
			407.3	359.2	30	27
49	维吉尼霉素 M1	正离子	526.2	508.3	90	18
			526.2	355.1	90	25
50	泰勒菌素	正离子	916.6	174	150	47
			916.6	772.5	150	43
51	恭夫西林	正离子	415.2	199.0	115	22
			415.2	170.9	115	53
52	青霉素G	正离子	367.3	160.0	30	21
			367.3	217.0	30	28
53	青霉素V	正离子	383.1	160.0	50	23
			383.1	114.0	50	54
54	氯唑西林	正离子	436.2	160.1	60	18
			436.2	277.1	60	18
55	苯唑西林	正离子	434.2	160.0	20	24
			434.2	144.0	20	40
56	氯霉素	负离子	320.9	152	-75	-24
			320.9	257	-75	-17
57	氟苯尼考	负离子	356	119	-80	-23
			356	219.2	-80	-16

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内容提要

大体积进样直接检测水中247种PPCPs及农药残留的LC-MS/MS快速筛查和定量方法

A Rapid Screening and Quantitative LC-MS/MS Method of 247 PPCPs and Pesticide Residues in Water by Large Volume Injection

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Key Words : LC-MS/MS, pesticide residues, PPCPs, large volume injection, QTRAP® 6500+

近年来，随着水环境的污染状况越来越重，人们对如何把控及监测水环境中的污染物也越来越关注。由于水环境中的污染物（主要来源为农药残留及药物和个人护理用品PPCPs）浓度低、检测难度大，因此往往需要将样品浓缩后再进行液质分析。主要的样品浓缩方法且为国标中应用较广的方法有液液萃取（Liquid-liquid extraction, LLE）和固相（Solid-phase extract, SPE），但LLE和SPE前处理方法都有耗时、消耗大量有毒试剂、精密度和准确度较差的缺点。

本文主要针对水环境中PPCPs及农药残留问题，在QTRAP® 6500+ LC-MS/MS系统上，采用大体积进样（Large Volume Injection, LVI）的方式，建立了247种化合物的快速筛查和定量方法，与国标LLE和SPE方法相比，LVI法具有简单、快速、绿色、精密度高、准确度高、消耗样品量小的优点，为水环境中PPCPs及农药残留问题提供了简单快速的解决方案。

本方法具有以下特点：

1. 本方法分析化合物种类多，包括农药、磺胺类、喹诺酮类、四环素类、β-内酰胺类、大环内酯类、激素类、精神类等16类化合物
2. 本方法采用一针进样智能化分时间段MRM（*Scheduled* MRM）、正负离子同时检测247种农药，分析时间仅13.5分钟，大大提高了通量
3. 本方法提供了247种化合物的质谱条件、液相条件以及保留时间，大大节省方法开发时间，提高工作效率
4. 本方法灵敏度高，重现性好，保证筛查和定量结果的准确性
5. 样品前处理简单、水样品直接进样，无需富集，简单、快速，省时、省力

仪器设备

SCIEX ExionLC™系统 + QTRAP® 6500+系统

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内容提要

样品前处理

水样直接进样分析

液相方法

色谱柱：Phenomenex Kinetex F5
（50 × 3.0 mm, 2.6 µm ）

流动相：A：水（0.1%甲酸）；
B：乙腈（0.1%甲酸）

流速：0.4 mL/min；

柱温：40 ℃；

进样量：100 µL

梯度洗脱

Time（min）	A (%)	B (%)
0.00	97	3
1.00	97	3
1.10	85	15
9.50	25	75
9.60	5	95
11.5	5	95
11.6	97	3
13.5	97	3

质谱方法

离子源：ESI源，正/负离子模式

离子源参数：

IS电压: 5500/-4500 V　　气帘气 CUR: 30 psi

雾化气 GS1: 50 psi　　辅助气 GS2: 60 psi

源温度 TEM: 500 ℃　　碰撞气 CAD: Medium

备注：各化合物质谱参数见附表1

表1. 自来水、市售矿泉水及添加样品测定结果（以氟康唑为例）。

Sample Name	Sample Type	Component Name	Actual Concentration	Area	Retention Time	Used	Calculated Concentration	Accuracy
BLANK	Blank	Fluconazole 1	N/A	N/A	N/A	☑	N/A	N/A
0.001ppb	Standard	Fluconazole 1	0.001	1.964e3	3.96	☑	0.0010	99.14
0.01ppb	Standard	Fluconazole 1	0.010	1.577e4	3.96	☑	0.0107	107.17
0.05ppb	Standard	Fluconazole 1	0.050	7.563e4	3.97	☑	0.0529	105.76
0.1ppb	Standard	Fluconazole 1	0.100	1.466e5	3.97	☑	0.1029	102.87
0.5ppb	Standard	Fluconazole 1	0.500	7.031e5	3.98	☑	0.4949	98.98
1ppb	Standard	Fluconazole 1	1.000	1.422e6	3.96	☑	1.0015	100.15
5ppb	Standard	Fluconazole 1	5.000	6.745e6	3.96	☑	4.7505	95.01
10ppb	Standard	Fluconazole 1	10.000	1.291e7	3.98	☑	9.0915	90.91
solvent	Solvent	Fluconazole 1	N/A	N/A	N/A	☑	N/A	N/A
Blank+0.001ppb	Quality Control	Fluconazole 1	0.001	1.819e3	3.99	☑	0.0009	88.95
Blank+0.01ppb	Quality Control	Fluconazole 1	0.010	1.448e4	3.99	☑	0.0098	98.10
Mineral water	Unknown	Fluconazole 1	N/A	N/A	N/A	☑	N/A	N/A
Tap water	Unknown	Fluconazole 1	N/A	N/A	N/A	☑	N/A	N/A
Tap water+0.001ppb	Quality Control	Fluconazole 1	0.001	2.142e3	3.97	☑	0.0011	111.72
Tap water+0.01ppb	Quality Control	Fluconazole 1	0.010	1.655e4	3.97	☑	0.0113	112.63
Mineral water+0.001ppb	Quality Control	Fluconazole 1	0.001	2.147e3	4.02	☑	0.0011	112.07
Mineral water+0.01ppb	Quality Control	Fluconazole 1	0.010	1.529e4	3.99	☑	0.0104	103.75

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内容提要

实验结果

1. 247种农药的典型色谱图

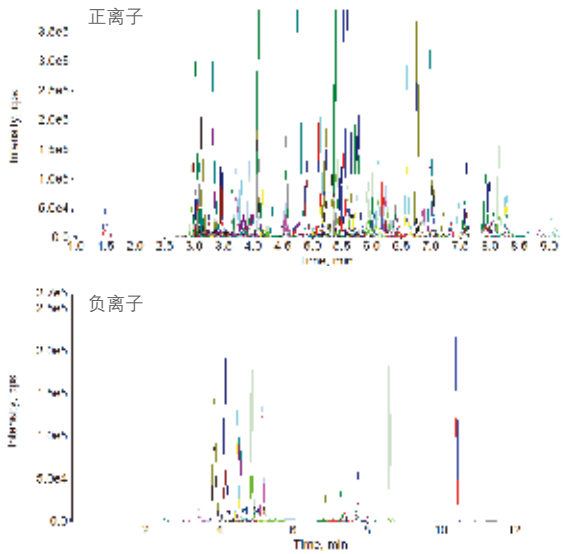

图1. 水中247种PPCPs及农药的色谱图（0.1 µg/L）。

2. 该方法有81.8%的化合物的定量限为0.01 µg/L，32.4%的化合物的定量限为0.001 µg/L，灵敏度高，重现性好，可用于实际水质样品的测定。

   备注：各化合物定量限和重现性见附表2

3. 实际样品测定：通过该方法分别对自来水、市售某品牌矿泉水及空白水添加一定浓度化合物的样品进行筛查和定量，结果表明：自来水和市售矿泉水水中均未检测出残留。添加一定浓度的样品的准确度在85%~115%之间，说明该方法准确可靠。

总结

本方法针对水环境中有机污染物残留问题，采用大体积进样的方式，在QTRAP® 6500+系统上建立了一套测定水中247种PPCPs和农药的LC-MS/MS快速筛查和定量检测方法。该方法分析时间仅为13.5分钟且样品无需前处理直接进样分析，节约时间和金钱成本。该方法灵敏度高，重现性好，可用于实际水环境中PPCPs和农药的准确测定，为水环境的把控和监测保驾护航。

附表1. 247种化合物的质谱参数和保留时间。

Q1	Q3	RT	Name
181.0	123.9	3.11	1,7 Dimethylxanthine 1
181.0	69.0	3.11	1,7 Dimethylxanthine 2
160.0	87.9	2.90	2-(4-Chlorophenoxy)-2-Methylpropionic Acid 1
160.0	116.8	2.90	2-(4-Chlorophenoxy)-2-Methylpropionic Acid 2
160.0	130.0	2.90	2-(4-Chlorophenoxy)-2-Methylpropionic Acid 3
194.1	137.1	6.65	2,3,5 TRIMETHACARB 1
194.1	122.0	6.65	2,3,5 TRIMETHACARB 2
190.0	173.0	3.46	2,6 Dichlorbenzamid 1
190.0	145.0	3.46	2,6 Dichlorbenzamid 2
291.1	179.0	10.84	2-Ethylhexyl 4-Methoxycinnamate 1
291.1	161.0	10.84	2-Ethylhexyl 4-Methoxycinnamate 2
291.1	133.0	10.84	2-Ethylhexyl 4-Methoxycinnamate 3
238.1	181.1	4.03	3 Hydroxycarbofuran 1
238.1	163.0	4.03	3 Hydroxycarbofuran 2
461.2	426.2	3.55	4 Epioxytetracycline 1
461.2	443.2	3.55	4 Epioxytetracycline 2
445.1	410.1	3.76	4 Epitetracycline 1
445.1	427.1	3.76	4 Epitetracycline 2
246.0	228.0	11.84	4-Acetylaminoantipyrine 1
246.0	104.0	11.84	4-Acetylaminoantipyrine 2
152.1	109.9	3.04	Acetaminophen 1
152.1	93.0	3.04	Acetaminophen 2
116.1	89.0	5.00	Aldicarb 1
116.1	70.0	5.00	Aldicarb 2
309.1	281.1	6.11	Alprazolam 1
309.1	205.0	6.11	Alprazolam 2
228.0	186.0	4.98	Ametryn 1
228.0	96.0	4.98	Ametryn 2
232.0	96.9	3.12	Aminophenazone 1
232.0	113.0	3.12	Aminophenazone 2
409.1	294.1	6.02	Amlodipine 1
409.1	237.8	6.02	Amlodipine 2

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附表1. 247种化合物的质谱参数和保留时间。（续）

Q1	Q3	RT	Name
366.2	113.9	5.41	Amoxicillin 1
366.2	208.0	5.41	Amoxicillin 2
382.3	333.0	5.91	Ampicillin +CH_3OH 1
382.3	160.0	5.91	Ampicillin +CH_3OH 2
350.2	106.0	3.30	Ampicillin +H 1
350.2	160.0	3.30	Ampicillin +H 2
146.0	117.0	1.52	Anhydroerythromycin A 1
146.0	66.0	1.52	Anhydroerythromycin A 2
146.0	53.9	1.52	Anhydroerythromycin A 3
267.1	144.9	3.03	Atenolol 1
267.1	190.0	3.03	Atenolol 2
198.0	156.0	3.35	Atrazin 2 hydroxy 1
198.0	86.0	3.35	Atrazin 2 hydroxy 2
375.4	591.5	4.21	Azithromycin 1
375.4	158.1	4.21	Azithromycin 2
224.1	167.0	5.98	Bendiocarb 1
224.1	109.0	5.98	Bendiocarb 2
308.2	115.9	4.99	Betaxolol 1
308.2	97.9	4.99	Betaxolol 2
362.0	139.0	7.01	Bezafibrate 1
362.0	316.1	7.01	Bezafibrate 2
326.1	116.1	4.42	Bisoprolol 1
326.1	89.0	4.42	Bisoprolol 2
343.0	307.0	7.71	Boscalid 1
343.0	140.0	7.71	Boscalid 2
261.0	205.0	4.15	Bromacil 1
261.0	188.0	4.15	Bromacil 2
195.0	138.0	3.38	Caffeine 1
195.0	110.0	3.38	Caffeine 2
263.2	231.0	3.51	Carbadox 1
263.2	145.0	3.51	Carbadox 2
237.0	193.9	5.37	Carbamazepine 1
237.0	192.9	5.37	Carbamazepine 2
214.0	157.0	6.89	Carbanolate 1
214.0	121.0	6.89	Carbanolate 2
202.1	145.0	6.35	Carbaryl 1
202.1	127.0	6.35	Carbaryl 2
237.0	118.0	5.17	Carbetamid 1
237.0	192.0	5.17	Carbetamid 2
364.0	114.0	3.01	Cefadroxil 1
364.0	208.0	3.01	Cefadroxil 2
463.0	347.0	4.61	Cefamandole lithium 1
463.0	158.1	4.61	Cefamandole lithium 2
424.1	292.0	3.12	Cefapirin 1
424.1	152.0	3.12	Cefapirin 2
454.9	323.0	3.72	Cefazolin 1
454.9	155.8	3.72	Cefazolin 2
512.0	240.9	6.39	Cefetamet pivoxyl 1
512.0	125.9	6.39	Cefetamet pivoxyl 2
456.0	166.9	3.50	Cefotaxime 1
456.0	125.0	3.50	Cefotaxime 2
348.0	157.9	3.28	Cephalexin 1
348.0	174.0	3.28	Cephalexin 2
350.0	175.9	3.37	Cephradine 1
350.0	157.9	3.37	Cephradine 2
716.4	558.3	5.69	Chloridazon-Methyl-Desphenyl 1
716.4	158.0	5.69	Chloridazon-Methyl-Desphenyl 2
291.0	72.0	7.60	Chloroxuron 1
291.0	218.0	7.60	Chloroxuron 2
479.1	462.0	4.44	Chlortetracycline 1
479.1	444.0	4.44	Chlortetracycline 2
213.0	72.0	6.05	Chlortoluron 1
213.0	46.0	6.05	Chlortoluron 2
253.2	159.0	2.74	Cimetidine 1
253.2	95.0	2.74	Cimetidine 2
263.1	217.1	4.68	Cinoxacin 1
263.1	189.0	4.68	Cinoxacin 2
332.1	288.1	3.82	Ciprofloxacin 1
332.1	245.1	3.82	Ciprofloxacin 2
748.5	590.4	6.33	Clarithromycin 1
748.5	158.0	6.33	Clarithromycin 2
277.0	203.0	4.09	Clenbuterol 1
277.0	168.1	4.09	Clenbuterol 2
293.0	196.9	6.21	Climbazole 1
293.0	140.9	6.21	Climbazole 2
366.2	305.1	4.13	Clinafloxacin 1
366.2	236.1	4.13	Clinafloxacin 2
425.3	126.1	4.34	Clindamycin 1
425.3	377.1	4.34	Clindamycin 2
316.1	270.0	6.02	Clonazepam 1
316.1	214.0	6.02	Clonazepam 2
250.0	169.0	4.06	Clothianidin 1
250.0	132.1	4.06	Clothianidin 2
436.1	160.0	6.82	Cloxacillin +H 1
436.1	277.0	6.82	Cloxacillin +H 2
468.2	160.0	6.82	Cloxacillin+CH_3OH 1
468.2	178.0	6.82	Cloxacillin+CH_3OH 2
300.2	215.0	3.19	Codeine 1
300.2	152.0	3.19	Codeine 2
361.2	163.2	5.15	Cortisone 1
361.2	121.1	5.15	Cortisone 2
177.0	80.0	1.36	Cotinine 1
177.0	98.0	1.36	Cotinine 2
254.0	198.0	5.83	Cybutryn 1
254.0	83.0	5.83	Cybutryn 2
292.0	125.0	6.98	Cyproconazol 1

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内容提要

附表1. 247种化合物的质谱参数和保留时间。（续）

Q1	Q3	RT	Name
292.0	70.0	6.98	Cyproconazol 2
345.0	284.0	6.94	Dehydronifedipine 1
345.0	268.0	6.94	Dehydronifedipine 2
414.0	240.9	3.07	Desacetylcefotaxime 1
414.0	124.9	3.07	Desacetylcefotaxime 2
170.1	128.1	4.84	Desethyl atrazin 2 hydroxy 1
170.0	86.0	4.84	Desethyl atrazin 2 hydroxy 2
145.9	104.0	0.00	Desethyl desisopropyl atrazin 1
145.9	105.5	0.00	Desethyl desisopropyl atrazin 2
188.0	146.0	3.99	Desethylatrazin 1
188.0	104.0	3.99	Desethylatrazin 2
202.0	146.0	5.30	Desethylsebuthylazin 1
202.0	104.0	5.30	Desethylsebuthylazin 2
202.0	146.0	5.31	Desethylterbutylazin 1
204.0	148.0	5.31	Desethylterbutylazin 2
174.0	104.0	3.50	Desisopropylatrazin 1
174.0	96.0	3.50	Desisopropylatrazin 2
219.0	127.0	6.16	Desmethyl Isoproturon 1
219.0	162.0	6.16	Desmethyl Isoproturon 2
272.2	171.0	5.09	Dextromethorphan 1
272.2	215.1	5.09	Dextromethorphan 2
614.6	360.8	0.58	Diatrizoic Acid 1
614.6	233.0	0.58	Diatrizoic Acid 2
285.1	154.0	6.43	Diazepam 1
285.1	193.0	6.43	Diazepam 2
470.1	160.1	6.84	Dicloxacillin 1
470.1	311.1	6.84	Dicloxacillin 2
400.1	356.1	4.53	Difloxacin 1
400.1	299.1	4.53	Difloxacin 2
391.2	355.2	4.13	Digoxigenin 1
391.2	337.2	4.13	Digoxigenin 2
651.3	97.1	5.15	Digoxin+H 1
781.3	651.3	5.15	Digoxin+H 2
415.1	178.0	5.62	Diltiazem 1
415.1	149.8	5.62	Diltiazem 2
327.0	205.0	8.35	Dimoxystrobin 1
256.1	167.0	5.42	Diphenhydramine 1
256.1	164.9	5.42	Diphenhydramine 2
255.0	180.9	3.13	Diprophylline 1
255.0	124.0	3.13	Diprophylline 2
280.1	107.0	5.69	Doxepin 1
280.1	165.0	5.69	Doxepin 2
445.0	428.1	4.75	Doxycycline 1
445.0	154.1	4.75	Doxycycline 2
321.0	234.0	3.61	Enoxacin 1
321.0	277.0	3.61	Enoxacin 2
360.0	316.1	4.07	Enrofloxacin 1
360.0	245.1	4.07	Enrofloxacin 2

Q1	Q3	RT	Name
330.0	121.0	7.73	Epoxyconazol 1
332.0	121.0	7.73	Epoxyconazol 2
716.5	158.0	5.75	Erythromucin H2O 2
734.5	576.4	5.47	Erythromycin 1
734.5	158.0	5.47	Erythromycin 2
716.5	558.4	5.75	Erythromycin H2O 1
255.1	159.1	6.44	Estradiol 1
255.1	133.2	6.44	Estradiol 2
271.0	132.9	7.20	Estronel 1
271.0	159.0	7.20	Estronel 2
287.0	121.0	8.21	Ethofumesat 1
287.0	259.0	8.21	Ethofumesat 2
208.1	95.0	7.16	Fenobucarb 1
208.1	152.0	7.16	Fenobucarb 2
302.0	88.0	8.19	Fenoxycarb 1
302.0	116.0	8.19	Fenoxycarb 2
165.0	72.0	3.99	Fenuron 1
165.0	46.0	3.99	Fenuron 2
307.0	220.1	3.96	Fluconazole 1
307.0	237.9	3.96	Fluconazole 2
364.0	194.0	8.38	Flufenacet 1
364.0	152.0	8.38	Flufenacet 2
262.1	202.1	5.86	Flumequin 1
262.1	174.0	5.86	Flumequin 2
310.2	148.0	6.69	Fluoxetine 1
310.2	91.0	6.69	Fluoxetine 2
316.0	165.0	8.11	Flusilazol 1
316.0	247.0	8.11	Flusilazol 2
345.2	121.0	4.02	Formoterol 1
345.2	148.8	4.02	Formoterol 2
494.2	369.0	7.93	Glibenclamide 1
494.2	169.0	7.93	Glibenclamide 2
324.1	126.9	7.12	Gliclazide 1
324.1	109.8	7.12	Gliclazide 2
491.2	352.0	7.91	Glimepiride 1
491.2	126.2	7.91	Glimepiride 2
446.2	321.2	6.37	Glipizide 1
446.2	103.0	6.37	Glipizide 2
363.2	105.0	5.00	Hydrocortisone 1
363.2	121.1	5.00	Hydrocortisone 2
281.0	85.9	6.12	Imipramine 1
281.0	193.0	6.12	Imipramine 2
508.0	167.0	7.41	Iodosulfuron methyl 1
508.0	141.0	7.41	Iodosulfuron methyl 2
429.2	207.1	6.09	Irbesartan 1
429.2	195.0	6.09	Irbesartan 2
194.0	95.0	6.55	Isoprocarb 1
194.0	152.0	6.55	Isoprocarb 2

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附表1. 247种化合物的质谱参数和保留时间。（续）

Q1	Q3	RT	Name
207.0	72.0	6.21	Isoproturon 1
207.0	165.0	6.21	Isoproturon 2
314.0	116.0	8.54	Kresoxim methyl 1
314.0	267.0	8.54	Kresoxim methyl 2
313.2	91.0	7.12	Levonorgestrel 1
313.2	245.2	7.12	Levonorgestrel 2
235.1	85.9	3.62	Lidocaine 1
235.1	99.0	3.62	Lidocaine 2
407.3	126.1	3.20	Lincomycin 1
407.3	359.2	3.20	Lincomycin 2
249.0	160.0	7.46	Linuron 1
249.0	182.0	7.46	Linuron 2
352.0	265.0	3.91	Lomefloxacin 1
352.0	308.1	3.91	Lomefloxacin 2
321.1	275.1	5.74	Lorazepam 1
321.1	229.1	5.74	Lorazepam 2
423.1	206.9	6.06	Losartan 1
423.1	179.9	6.06	Losartan 2
387.1	327.3	8.33	Medroxyprogesterone 17 acetate 1
387.1	123.0	8.33	Medroxyprogesterone 17 acetate 2
343.2	187.1	7.22	Megestrol 1
343.2	267.2	7.22	Megestrol 2
226.1	169.0	7.33	Mercaptodimethur 1
226.1	121.0	7.33	Mercaptodimethur 2
280.0	160.0	6.11	Metalaxyl 1
280.0	220.0	6.11	Metalaxyl 2
222.0	165.0	5.88	Methabenzthiazuron 1
222.0	150.0	5.88	Methabenzthiazuron 2
163.0	88.0	3.48	Methomyl 1
163.0	106.0	3.48	Methomyl 2
106.1	58.0	2.37	Methomyl oxime 1
106.1	88.0	2.37	Methomyl oxime 2
303.2	109.0	6.80	Methyltestosterone 1
303.2	97.0	6.80	Methyltestosterone 2
259.0	170.0	6.58	Metobromuron 1
259.0	148.0	6.58	Metobromuron 2
166.0	109.0	5.40	Metocarb 1
166.0	94.0	5.40	Metocarb 2
268.1	116.0	3.87	Metoprolol 1
268.1	159.0	3.87	Metoprolol 2
382.0	167.0	6.13	Metsulfuron methyl 1
382.0	199.0	6.13	Metsulfuron methyl 2
225.0	127.0	4.60	Mevinphos 1
225.0	193.0	4.60	Mevinphos 2
416.9	158.8	8.04	Miconazole 1
416.9	160.9	8.04	Miconazole 2
326.1	291.1	5.16	Midazolam 1
326.1	249.0	5.16	Midazolam 2

Q1	Q3	RT	Name
215.0	126.0	6.36	Monolinuron 1
215.0	148.0	6.36	Monolinuron 2
232.1	214.0	3.27	Mono-Methyl Terephthalate 1
232.1	103.9	3.27	Mono-Methyl Terephthalate 2
296.0	134.0	5.00	N-Acetyl Sulfamethoxazole 1
296.0	198.0	5.00	N-Acetyl Sulfamethoxazole 2
310.1	254.1	3.32	Nadolol 1
310.1	201.0	3.32	Nadolol 2
415.2	199.0	5.65	Nafcillin 1
415.2	170.9	5.65	Nafcillin 2
233.0	187.0	5.42	Nalidixic acid 1
233.0	159.0	5.42	Nalidixic acid 2
282.2	236.1	5.64	Nitrazepam 1
282.2	180.0	5.64	Nitrazepam 2
299.2	231.2	6.55	Norethindrone 1
299.2	109.1	6.55	Norethindrone 2
320.1	276.1	3.73	Norfloxacin 1
320.1	233.1	3.73	Norfloxacin 2
370.2	91.1	8.26	Norgestimate 1
370.2	124.0	8.26	Norgestimate 2
362.2	318.1	3.76	Ofloxacin 1
362.2	261.1	3.76	Ofloxacin 2
688.4	158.2	5.06	Oleandomycin 1
688.4	544.3	5.06	Oleandomycin 2
396.0	352.0	4.14	Orbifloxacin 1
396.0	295.2	4.14	Orbifloxacin 2
275.2	259.1	3.66	Ormetoprim 1
275.2	123.0	3.66	Ormetoprim 2
434.2	160.0	6.61	Oxacillin +CH_3OH 1
434.2	144.0	6.61	Oxacillin +CH_3OH 2
402.2	160.0	6.43	Oxacillin +H 1
402.2	243.0	6.43	Oxacillin +H 2
287.1	241.0	5.58	Oxazepam 1
287.1	269.0	5.58	Oxazepam 2
262.0	216.1	4.95	Oxolinic acid 1
262.0	160.0	4.95	Oxolinic acid 2
461.2	426.2	3.55	Oxytetracycline 1
461.2	426.2	3.58	Oxytetracycline 1
461.2	443.2	3.55	Oxytetracycline 2
461.2	443.2	3.58	Oxytetracycline 2
334.1	316.1	3.81	Pefloxacin 1
334.1	290.2	3.81	Pefloxacin 2
367.3	160.0	5.41	Penicillin G +CH_3OH 1
367.3	217.0	5.41	Penicillin G +CH_3OH 2
335.2	176.0	5.52	Penicillin G +H 1
335.2	160.0	5.52	Penicillin G +H 2
383.1	160.0	5.90	Penicillin V+CH_3OH 1
383.1	114.0	5.90	Penicillin V+CH_3OH 2

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附表1. 247种化合物的质谱参数和保留时间。（续）

Q1	Q3	RT	Name
351.2	160.0	5.90	Penicillin V+H 1
351.2	114.0	5.90	Penicillin V+H 2
180.1	138.0	4.49	Phenacetin 1
180.1	110.0	4.49	Phenacetin 2
189.0	104.0	3.75	Phenazone 1
189.0	130.0	3.75	Phenazone 2
301.1	168.0	7.45	Phenmedipham 1
301.0	136.0	7.45	Phenmedipham 2
368.0	182.0	9.16	Phosalon 1
368.0	111.0	9.16	Phosalon 2
299.0	129.0	9.21	Phoxim 1
299.0	77.0	9.21	Phoxim 2
368.0	205.0	9.09	Picoxystrobin 1
386.0	145.0	9.09	Picoxystrobin 2
359.2	147.2	5.10	Prednisone 1
359.2	341.2	5.10	Prednisone 2
376.0	308.1	7.30	Prochloraz 1
376.0	266.1	7.30	Prochloraz 2
208.1	151.1	7.43	Promecarb 1
208.1	109.0	7.43	Promecarb 2
242.0	158.0	5.60	Prometryn 1
242.0	200.0	5.60	Prometryn 2
189.0	102.0	3.07	Propamocarb 1
189.0	74.0	3.07	Propamocarb 2
212.0	128.0	3.75	Propazin 2 hydroxy 1
212.0	170.0	3.75	Propazin 2 hydroxy 2
210.0	111.0	5.76	Propoxur 1
210.0	168.0	5.76	Propoxur 2
231.1	189.1	5.62	Propyphenazone 1
231.1	201.0	5.62	Propyphenazone 2
271.0	180.1	3.95	Rac Trans-10,11-Dihydro-10,11-Dihydroxy Carbamazepine 1
271.0	210.0	3.95	Rac Trans-10,11-Dihydro-10,11-Dihydroxy Carbamazepine 2
315.1	176.0	3.09	Ranitidine 1
315.1	101.9	3.09	Ranitidine 2
453.3	230.2	6.64	Repaglinde 1
453.3	162.0	6.64	Repaglinde 2
837.6	679.5	6.41	Roxithromycin 1
837.6	158.1	6.41	Roxithromycin 2
240.2	148.1	2.90	Salbutamol 1
240.2	166.0	2.90	Salbutamol 2
386.0	342.3	4.43	Sarafloxacin 1
386.0	299.0	4.43	Sarafloxacin 2
230.0	174.0	6.86	Sebutylazin 1
230.0	104.0	6.86	Sebutylazin 2
475.2	283.1	5.34	Sildenafil 1
475.2	58.0	5.34	Sildenafil 2
273.1	132.9	3.03	Sotalol 1
273.1	255.0	3.03	Sotalol 2
393.0	349.2	4.50	Sparfloxacin 1
393.0	292.0	4.50	Sparfloxacin 2
298.0	144.0	7.07	Spiroxamine 1
298.0	100.0	7.07	Spiroxamine 2
277.1	156.0	4.87	Sulfabenzamide 1
277.1	108.0	4.87	Sulfabenzamide 2
285.1	156.0	4.13	Sulfachloropyridazine 1
285.1	108.1	4.13	Sulfachloropyridazine 2
251.1	156.0	3.17	Sulfadiazine 1
251.1	92.0	3.17	Sulfadiazine 2
311.1	156.1	5.07	Sulfadimethoxine 1
311.1	218.0	5.07	Sulfadimethoxine 2
311.1	156.1	4.56	Sulfadoxine 1
311.1	108.2	4.56	Sulfadoxine 2
265.2	156.1	3.43	Sulfamerazine 1
265.2	172.1	3.43	Sulfamerazine 2
279.1	186.1	3.64	Sulfamethazine 1
279.1	156.0	3.64	Sulfamethazine 2
271.0	156.1	3.75	Sulfamethizole 1
271.0	108.0	3.75	Sulfamethizole 2
254.1	156.0	4.82	Sulfamethoxazole 1
254.1	108.0	4.82	Sulfamethoxazole 2
281.0	126.1	3.82	Sulfamethoxypyridazine 1
281.0	156.0	3.82	Sulfamethoxypyridazine 2
173.0	93.0	1.65	Sulfanilamide 1
173.0	76.0	1.65	Sulfanilamide 2
315.0	156.0	5.13	Sulfaphenazole 1
315.0	108.0	5.13	Sulfaphenazole 2
250.1	156.1	3.32	Sulfapyridine 1
250.1	108.0	3.32	Sulfapyridine 2
301.1	156.0	5.06	Sulfaquinoxaline 1
301.1	108.0	5.06	Sulfaquinoxaline 2
256.0	156.0	3.30	Sulfathiazole 1
256.0	108.0	3.30	Sulfathiazole 2
268.1	156.1	4.56	Sulfisoxazole 1
268.1	113.2	4.56	Sulfisoxazole 2
215.0	156.0	2.83	Sulphacetamide 1
215.0	108.0	2.83	Sulphacetamide 2
342.2	213.9	3.20	Sulpiride 1
342.2	111.8	3.20	Sulpiride 2
334.0	117.0	8.94	Tebufenpyrad 1
334.0	145.0	8.94	Tebufenpyrad 2
515.1	497.2	6.10	Telmisartan 1
515.1	276.1	6.10	Telmisartan 2
301.0	255.1	6.30	Temazepam 1
301.0	177.0	6.30	Temazepam 2
226.0	170.0	4.82	Terbumeton 1
226.0	114.0	4.82	Terbumeton 2

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附表1. 247种化合物的质谱参数和保留时间。（续）

Q1	Q3	RT	Name
212.0	156.0	3.83	Terbuthylazin 2 hydroxy 1
212.0	114.0	3.83	Terbuthylazin 2 hydroxy 2
184.0	128.0	2.99	Terbuthylazin desethyl 2 hydroxy 1
184.0	86.0	2.99	Terbuthylazin desethyl 2 hydroxy 2
242.0	186.0	5.68	Terbutryn 1
242.0	96.0	5.68	Terbutryn 2
230.0	174.0	6.86	Terbutylazin 1
230.0	104.0	6.86	Terbutylazin 2
289.2	97.2	6.49	Testosterone 1
289.2	109.1	6.49	Testosterone 2
345.2	97.0	8.96	Testosterone propionate 1
345.2	109.0	8.96	Testosterone propionate 2
445.1	410.1	3.75	Tetracycline 1
445.1	410.2	3.81	Tetracycline 1
445.1	427.1	3.75	Tetracycline 2
445.1	427.1	3.81	Tetracycline 2
202.2	175.0	3.34	Thiabendazole 1
202.2	130.9	3.34	Thiabendazole 2
388.0	205.0	5.81	Thifensulfuron methyl 1
388.0	167.0	5.81	Thifensulfuron methyl 2
869.5	696.5	5.17	Tilmicosin 1
869.5	174.2	5.17	Tilmicosin 2
271.1	155.0	6.20	Tolbutamide 1
271.1	91.1	6.20	Tolbutamide 2
364.0	334.0	4.25	Topramezone 1
364.0	125.0	4.25	Topramezone 2
271.2	199.1	5.89	Trenbolone 1
271.2	165.0	5.89	Trenbolone 2
295.0	135.0	5.47	Triamiphos 1
295.0	44.0	5.47	Triamiphos 2
343.1	308.1	6.24	Triazolam 1
343.1	239.0	6.24	Triazolam 2
396.0	155.0	7.15	Tribenuron methyl 1
396.0	155.0	7.32	Tribenuron methyl 1
396.0	181.0	7.15	Tribenuron methyl 2
396.0	181.0	7.32	Tribenuron methyl 2
315.1	126.8	9.12	Triclocarban 1
315.1	92.9	9.12	Triclocarban 2
493.0	264.0	8.26	Triflusulfuron methyl 1
493.0	96.0	8.26	Triflusulfuron methyl 2
291.1	230.1	3.46	Trimethoprim 1
291.1	123.1	3.46	Trimethoprim 2
436.2	206.9	7.19	Valsartan 1
436.2	235.0	7.19	Valsartan 2
824.3	205.0	7.68	Virginiamycin S1 1
824.3	663.2	7.68	Virginiamycin S1 2
526.2	508.3	6.24	Virginiamycins M1 1
526.2	355.1	6.24	Virginiamycins M1 2
309.1	162.8	7.00	Warfarin 1
309.1	251.1	7.00	Warfarin 2
308.1	235.0	4.39	Zolpidem 1
308.1	263.0	4.39	Zolpidem 2
253.0	195.0	4.94	2,4,5-T 1
255.0	197.0	4.94	2,4,5-T 2
267.0	195.0	5.56	2,4,5-TP 1
269.0	197.0	5.56	2,4,5-TP 2
219.0	161.0	4.22	2,4-D 1
221.0	163.0	4.22	2,4-D 2
161.0	125.0	7.29	2,4-DB 1
247.0	161.0	7.29	2,4-DB 2
233.0	161.0	4.87	2,4-DP 1
235.0	163.0	4.87	2,4-DP 2
219.2	200.6	4.91	2,6-Di-tert-butyl-4-methylphenol 1
219.2	172.7	4.91	2,6-Di-tert-butyl-4-methylphenol 2
294.0	250.0	7.46	Diclofenac Acid 1
294.0	214.0	7.46	Diclofenac Acid 2
295.1	144.8	7.05	Ethinylestradiol 1
295.1	267.0	7.05	Ethinylestradiol 2
462.8	415.8	10.42	Fluazinam 1
462.8	397.8	10.42	Fluazinam 2
249.2	121.0	8.60	Gemfibrozil 1
249.2	106.0	8.60	Gemfibrozil 2
205.1	159.0	7.75	Ibuprofen 1
205.1	161.0	7.75	Ibuprofen 2
775.8	126.8	2.46	Iomeprol 1
789.8	126.7	3.00	Iopromide 1
199.0	141.0	4.51	MCPA 1
201.0	143.0	4.51	MCPA 2
227.0	141.0	7.39	MCPB 1
229.0	143.0	7.39	MCPB 2
213.0	141.0	5.25	MCPP 1
215.0	143.0	5.25	MCPP 2
179.0	119.9	3.66	Mono-Methyl Terephthalate 1
179.0	75.9	3.66	Mono-Methyl Terephthalate 2
229.1	169.0	6.88	Naproxen 1
229.1	141.1	6.88	Naproxen 2
287.0	35.0	9.22	Triclosan 1
289.0	35.0	9.22	Triclosan 2

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附表2. 247种化合物的线性、定量限和重现性。

中文名	英文名	线性	r	定量限	RSD%
1,7-二甲基黄嘌呤	1,7 Dimethylxanthine	0.001-10	0.99759	0.001	1.2
2-(4-氯苯氧基)-2-甲基丙酸	2-(4-Chlorophenoxy)-2-Methylpropionic Acid	0.05-10	0.99507	0.05	9.0
混杀威	2,3,5 Trimethacarb	0.005-5	0.99576	0.005	5.4
2,4,5-三氯苯氧乙酸	2,4,5-T	0.01-10	0.99776	0.01	9.7
2,4,5-滴丙酸	2,4,5-TP	0.005-10	0.99694	0.005	2.4
2,4-二氯苯氧乙酸	2,4-D	0.005-50	0.99551	0.005	4.7
4-（2,4-二氯苯氧）-丁酸	2,4-DB	0.005-100	0.99544	0.005	5.2
2,4-滴丙酸	2,4-DP	0.005-100	0.99627	0.005	3.5
2,6-二氯苯甲酰胺	2,6 Dichlorbenzamid	0.01-10	0.99465	0.01	4.2
2,6-二叔丁基对甲酚(BHT)	2,6-Di-tert-butyl-4-methylphenol	0.05-100	0.99378	0.05	8.4
甲氧基肉桂酸辛酯;对甲氧基肉桂酸-2-乙基己酯	2-Ethylhexyl 4-Methoxycinnamate	0.1-10	0.99395	0.1	5.2
3-羟基呋喃丹	3 Hydroxycarbofuran	0.001-1	0.99414	0.001	2.9
4-差向土霉素	4 Epioxytetracycline	0.1-10	0.99443	0.1	9.7
4-差向四环素	4 Epitetracycline	0.1-10	0.99642	0.1	2.6
4-乙酰胺基安替比林	4-Acetylaminoantipyrine	1-100	0.99155	1	2.1
N-乙酰对氨基酚	Acetaminophen	0.01-10	0.99336	0.01	10.1
涕灭威(铁灭克)	Aldicarb	0.005-5	0.99289	0.005	2.8
阿普唑仑	Alprazolam	0.01-10	0.9985	0.01	3.6
莠灭净	Ametryn	0.001-10	0.99556	0.001	6.4
氨基比林	Aminophenazone	0.001-1	0.9953	0.001	6.3
氨氯地平	Amlodipine	0.1-10	0.99648	0.1	6.3
阿莫西林	Amoxicillin	0.5-100	0.99713	0.5	8.4
氨苄青霉素 (安比西林)	Ampicillin +H	0.01-100	0.99163	0.01	6.5
脱氢红霉素 A	Anhydroerythromycin A	0.5-100	0.99339	0.5	5.8
阿替洛尔	Atenolol	0.001-1	0.99483	0.001	3.7
2-羟基阿特拉津	Atrazin 2 hydroxy	0.005-1	0.99625	0.005	9.4
阿奇霉素 (叠氮红霉素)	Azithromycin	0.005-1	0.99195	0.005	0.1
恶虫威	Bendiocarb	0.01-100	0.99276	0.01	4.6
倍他洛尔	Betaxolol	0.005-1	0.99509	0.005	4.6
苯扎贝特	Bezafibrate	0.005-100	0.99625	0.005	8.7
比索洛尔	Bisoprolol	0.01-10	0.99727	0.01	3.9
啶酰菌胺	Boscalid	0.01-10	0.99994	0.01	3.9
除草定	Bromacil	0.01-1	0.99193	0.01	1.2
咖啡因	Caffeine	0.01-10	0.99815	0.01	5.6
卡巴多, 卡巴氧	Carbadox	0.05-5	0.99329	0.05	8.4
卡马西平	Carbamazepine	0.001-1	0.99352	0.001	6.6
氯灭杀威	Carbanolate	0.005-100	0.99419	0.005	6.6
甲萘威	Carbaryl	0.01-10	0.99764	0.01	2.5
双酰草胺	Carbetamide	0.005-1	0.99299	0.005	8.0
头孢羟氨苄	Cefadroxil	0.05-10	0.99523	0.05	4.1
头孢孟多锂	Cefamandole lithium	0.1-100	0.99589	0.1	9.2
头孢匹啉	Cefapirin	0.01-10	0.99732	0.01	4.2
头孢唑啉	Cefazolin	0.01-10	0.99716	0.01	1.5
头孢他美酯	Cefetamet pivoxyl	0.001-10	0.99724	0.001	0.9
头孢噻肟	Cefotaxime	0.01-10	0.99602	0.01	4.2
头孢氨苄	Cephalexin	0.01-10	0.99203	0.01	8.2
头孢拉定	Cephradine	0.05-10	0.99437	0.05	6.5
脱苯基甲基氯草敏	Chloridazon-Methyl-Desphenyl	0.1-100	0.99675	0.1	4.6
枯草隆	Chloroxuron	0.001-5	0.99771	0.001	2.4
金霉素	Chlortetracycline	0.01-50	0.99592	0.01	5.8

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附表2. 247种化合物的线性、定量限和重现性。（续）

中文名	英文名	线性	r	定量限	RSD%
绿麦隆	Chlortoluron	0.001-1	0.99242	0.001	10.0
甲腈咪胺, 西咪替丁	Cimetidine	0.001-10	0.99474	0.001	5.9
西诺沙星	Cinoxacin	0.005-1	0.9931	0.005	7.6
环丙沙星	Ciprofloxacin	0.05-10	0.9908	0.05	8.6
甲红霉素 (克拉霉素)	Clarithromycin	0.01-10	0.99441	0.01	3.7
克仑特罗	Clenbuterol	0.001-1	0.99172	0.001	1.4
甘宝素	Climbazole	0.001-10	0.99605	0.001	7.2
克林沙星	Clinafloxacin	0.005-100	0.99515	0.005	0.8
克林霉素	Clindamycin	0.001-1	0.99027	0.001	9.1
氯硝西泮	Clonazepam	0.001-10	0.99846	0.001	3.2
克虫定，噻虫胺	Clothianidin	0.05-10	0.99177	0.05	4.8
邻氯青霉素	Cloxacillin+CH3OH	0.01-100	0.99581	0.01	3.0
可待因	Codeine	0.01-10	0.99176	0.01	8.1
可的松	Cortisone	0.05-10	0.99873	0.05	3.1
可替宁	Cotinine	0.001-10	0.99273	0.001	1.9
2-叔丁氨基-4-环丙氨基-6-甲硫基-s-三嗪	Cybutryn	0.001-1	0.99839	0.001	9.4
环唑醇	Cyproconazol	0.001-10	0.99965	0.001	1.3
脱氢硝苯地平	Dehydronifedipine	0.005-0.5	0.99543	0.005	2.3
3-去乙酰基头孢噻肟	Desacetylcefotaxime	0.05-10	0.9987	0.05	3.1
莠去津-脱乙基-二羟基	Desethyl atrazin 2 hydroxy	0.05-10	0.99202	0.05	7.9
莠去津-脱乙基-脱异丙基	Desethyl desisopropyl atrazin	1-10	0.99423	1	4.7
莠去津-脱乙基	Desethylatrazin	0.01-10	0.99358	0.01	2.4
去乙基顺丁烯二嗪	Desethylsebuthylazin	0.001-10	0.99569	0.001	0.6
特丁津-脱乙基	Desethylterbutylazine	0.001-10	0.99404	0.001	6.9
莠去津-脱异丙基	Desisopropyl atrazin	0.01-10	0.99647	0.01	2.1
1-(3.4-二氯苯基)-3-甲基脲（去甲基异丙隆）	Desmethyl Isoproturon	0.01-10	0.99422	0.01	7.3
右美沙芬	Dextromethorphan	0.01-5	0.99603	0.01	6.8
泛影酸	Diatrizoic Acid	0.01-10	0.99719	0.01	7.6
地西泮; 安定	Diazepam	0.001-5	0.99694	0.001	3.1
双氯芬酸	Diclofenac Acid	0.05-100	0.99205	0.05	1.6
双氯西林	Dicloxacillin	0.01-100	0.99644	0.01	10.1
双氟沙星	Difloxacin	0.01-10	0.99458	0.01	6.1
异羟基洋地黄毒甙元	Digoxigenin	0.05-5	0.99407	0.05	2.6
地高辛	Digoxin+H	0.5-100	0.99359	0.5	10.8
地尔硫卓	Diltiazem	0.005-5	0.99314	0.005	6.7
醚菌胺	Dimoxystrobin	0.005-1	0.99468	0.005	2.6
苯海拉明	Diphenhydramine	0.005-1	0.9963	0.005	5.2
二羟丙茶碱	Diprophylline	0.01-10	0.99849	0.01	3.1
多虑平	Doxepin	0.005-1	0.99775	0.005	4.7
强力霉素	Doxycycline	0.01-10	0.99383	0.01	1.9
依诺沙星	Enoxacin	0.05-10	0.99654	0.05	4.2
恩诺沙星	Enrofloxacin	0.001-10	0.99264	0.001	9.4
氟环唑	Epoxyconazol	0.001-10	0.99988	0.001	3.7
红霉素	Erythromycin	0.001-10	0.99113	0.001	6.1
脱水红霉素	Erythromycin H2O	0.01-50	0.99431	0.01	10.5
雌二醇; 17 β -雌二醇	Estradiol	0.01-10	0.99946	0.01	7.5
雌酮	Estronel	0.5-100	0.99587	0.5	8.1
炔雌醇	Ethinylestradiol	0.1-100	0.99628	0.1	5.2
乙氧呋草黄	Ethofumesat	0.05-10	0.99941	0.05	3.2
仲丁威	Fenobucarb	0.01-5	0.9946	0.01	8.2

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附表2. 247种化合物的线性、定量限和重现性。（续）

中文名	英文名	线性	r	定量限	RSD%
苯氧威	Fenoxycarb	0.05-10	0.99266	0.05	7.6
非草隆	Fenuron	0.1-10	0.99576	0.1	1.7
氟啶胺	Fluazinam	0.001-0.1	0.99401	0.001	2.2
氟康唑	Fluconazole	0.001-10	0.99801	0.001	1.5
氟噻草胺	Flufenacet	0.001-10	0.99968	0.001	8.3
氟甲喹	Flumequin	0.001-10	0.99589	0.001	2.5
氟西汀	Fluoxetine	0.01-100	0.99767	0.01	7.7
氟硅唑	Flusilazol	0.001-10	0.99479	0.001	6.8
福莫特罗	Formoterol	0.001-10	0.99484	0.001	6.8
吉非罗齐	Gemfibrozil	0.005-100	0.99697	0.005	8.4
格列本脲	Glibenclamide	0.001-10	0.99903	0.001	4.0
格列齐特	Gliclazide	0.005-1	0.99603	0.005	8.5
格列美脲	Glimepiride	0.001-10	0.99186	0.001	9.6
格列吡嗪	Glipizide	0.001-10	0.99983	0.001	1.4
氢化可的松	Hydrocortisone	0.05-10	0.99357	0.05	11.0
布洛芬	Ibuprofen	0.01-100	0.99582	0.01	7.9
丙咪嗪	Imipramine	0.005-1	0.9967	0.005	7.5
甲基碘磺隆	Iodosulfuron methyl	0.001-10	0.99529	0.001	7.4
碘美普尔	Iomeprol	0.005-100	0.99512	0.005	9.2
碘普罗胺	Iopromide	0.05-100	0.99468	0.05	6.1
厄贝沙坦	Irbesartan	0.001-1	0.99756	0.001	2.4
异丙威	Isoprocarb	0.05-10	0.99556	0.05	6.6
异丙隆	Isoproturon	0.001-1	0.9942	0.001	6.6
醚菌酯	Kresoxim methyl	0.01-10	0.99499	0.01	6.8
甲基炔酮, 左炔诺孕酮	Levonorgestrel	0.05-10	0.99767	0.05	9.9
利多卡因	Lidocaine	0.005-1	0.99208	0.005	7.4
林可霉素 (洁霉素)	Lincomycin	0.001-10	0.9984	0.001	8.4
利谷隆	Linuron	0.001-10	0.99608	0.001	9.6
洛美沙星, 罗米沙星	Lomefloxacin	0.01-10	0.9921	0.01	8.8
氯羟去甲安定、劳拉西泮	Lorazepam	0.01-10	0.99929	0.01	5.7
洛沙坦	Losartan	0.001-1	0.99514	0.001	2.5
2-甲基-4氯苯氧乙酸	MCPA	0.005-100	0.99854	0.005	5.6
4-（2-甲基-4-氯苯氧基）-丁酸	MCPB	0.01-10	0.99708	0.01	6.5
2-（2-甲基-4-氯苯氧基）-丙酸	MCPP	0.005-100	0.99839	0.005	10.3
安宫黄体酮 (醋酸甲孕酮)	Medroxyprogesterone 17 acetate	0.01-10	0.99745	0.01	6.1
甲地孕酮	Megestrol	0.01-10	0.99517	0.01	3.6
灭虫威 (甲硫威)	Mercaptodimethur	0.001-100	0.99279	0.001	5.9
甲霜灵	Metalaxyl	0.001-1	0.99735	0.001	2.0
甲基苯噻隆	Methabenzthiazuron	0.001-1	0.99677	0.001	10.6
灭多威	Methomyl	0.01-0.5	0.99444	0.01	0.1
灭多威肟	Methomyl oxime	0.01-50	0.99763	0.01	10.8
甲睾酮	Methyltestosterone	0.001-10	0.99796	0.001	6.5
溴谷隆	Metobromuron	0.01-10	0.99664	0.01	5.3
速灭威	Metocarb	0.005-10	0.99583	0.005	2.7
美托洛尔	Metoprolol	0.01-10	0.99503	0.01	6.0
甲磺隆	Metsulfuron methyl	0.001-10	0.99821	0.001	4.2
速灭磷	Mevinphos	0.01-10	0.99397	0.01	5.9
霉可唑 (咪康唑)	Miconazole	0.001-0.5	0.99394	0.001	10.1
咪哒唑仑	Midazolam	0.001-1	0.99622	0.001	8.4
绿谷隆	Monolinuron	0.01-1	0.99483	0.01	3.9

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附表2. 247种化合物的线性、定量限和重现性。（续）

中文名	英文名	线性	r	定量限	RSD%
对苯二甲酸单甲酯	Mono-Methyl Terephthalate	0.01-100	0.99817	0.01	1.3
对苯二甲酸单甲酯	Mono-Methyl Terephthalate	0.05-10	0.99862	0.05	3.2
醋磺胺甲噁唑	N-Acetyl Sulfamethoxazole	0.01-10	0.99518	0.01	1.6
纳多洛尔	Nadolol	0.005-0.5	0.99212	0.005	8.6
萘夫西林	Nafcillin	0.01-100	0.99428	0.01	4.5
萘啶酸	Nalidixic acid	0.001-1	0.99472	0.001	2.6
萘普生	Naproxen	0.005-10	0.99545	0.005	0.1
硝西泮	Nitrazepam	0.001-10	0.99989	0.001	2.6
炔诺酮	Norethindrone	0.01-10	0.99793	0.01	9.7
诺氟沙星	Norfloxacin	0.1-10	0.99273	0.1	4.3
诺孕酯	Norgestimate	0.5-10	0.99796	0.5	0.7
氧氟沙星	Ofloxacin	0.001-10	0.99441	0.001	7.1
竹桃霉素	Oleandomycin	0.005-10	0.99421	0.005	5.5
奥比沙星	Orbifloxacin	0.01-10	0.99403	0.01	7.7
奥美普林	Ormetoprim	0.005-0.5	0.99116	0.005	1.2
苯唑西林	Oxacillin +H	0.001-10	0.99517	0.001	8.1
奥沙西泮	Oxazepam	0.001-10	0.99743	0.001	3.2
恶喹酸 (奥索利酸)	Oxolinic acid	0.001-1	0.99691	0.001	2.1
地霉素(土霉素)	Oxytetracycline	0.01-10	0.99411	0.01	2.4
土霉素	Oxytetracycline	0.005-50	0.99272	0.005	3.9
培氟沙星	Pefloxacin	0.05-10	0.99404	0.05	5.5
盘尼西林G (青霉素)	Penicillin G +CH3OH	0.005-100	0.99286	0.005	0.6
苯氧甲基青霉素(青霉素V)	Penicillin V+CH3OH	0.001-100	0.99468	0.001	9.7
非那西丁	Phenacetin	0.01-1	0.99566	0.01	7.1
安替比林	Phenazone	0.001-1	0.9951	0.001	9.4
甜菜宁，苯敌草	Phenmedipham	0.001-5	0.99568	0.001	7.1
伏杀磷	Phosalon	0.001-10	0.9917	0.001	0.3
辛硫磷	Phoxim	0.001-10	0.99685	0.001	5.8
啶氧菌酯	Picoxystrobin	0.005-10	0.99721	0.005	9.3
泼尼松 (脱氢可的松)	Prednisone	0.05-10	0.99729	0.05	9.5
咪鲜胺	Prochloraz	0.05-10	0.99593	0.05	0.7
猛杀威	Promecarb	0.005-5	0.99503	0.005	0.6
扑草净	Prometryn	0.001-1	0.99434	0.001	0.1
霜霉威	Propamocarb	0.001-1	0.99618	0.001	1.7
扑灭津-2-羟基	Propazin 2 hydroxy	0.001-10	0.99861	0.001	8.1
残杀威	Propoxur	0.05-10	0.99458	0.05	0.9
异丙安替比林	Propyphenazone	0.01-10	0.99515	0.01	0.3
反式-10,11-二羟基-10,11-二氢卡马西平	Rac Trans-0,-Dihydro-0,-Dihydroxy Carbamazepine	0.01-1	0.9955	0.01	2.7
雷尼替丁(甲硝呋胍)	Ranitidine	0.01-1	0.99702	0.01	3.0
瑞格列奈	Repaglinde	0.01-10	0.99483	0.01	1.8
罗红霉素	Roxithromycin	0.01-10	0.99655	0.01	3.2
沙丁胺醇	Salbutamol	0.001-1	0.99354	0.001	6.2
沙拉沙星	Sarafloxacin	0.01-10	0.99547	0.01	3.9
另丁津	Sebutylazin	0.001-10	0.99583	0.001	2.3
西地那非	Sildenafil	0.005-10	0.99293	0.005	8.6
索他洛尔	Sotalol	0.001-1	0.99315	0.001	7.6
司帕沙星	Sparfloxacin	0.01-10	0.9926	0.01	5.3
螺环菌胺	Spiroxamine	0.01-10	0.99375	0.01	2.7
苯酰磺胺	Sulfabenzamide	0.001-10	0.99619	0.001	9.8

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附表2. 247种化合物的线性、定量限和重现性。（续）

中文名	英文名	线性	r	定量限	RSD%
磺胺氯哒嗪	Sulfachloropyridazine	0.01-10	0.99968	0.01	6.3
磺胺嘧啶 (磺胺哒嗪)	Sulfadiazine	0.01-10	0.99513	0.01	5.0
磺胺间二甲氧嘧啶	Sulfadimethoxine	0.001-10	0.99555	0.001	1.7
磺胺邻二甲氧嘧啶 (磺胺多辛)	Sulfadoxine	0.005-1	0.994	0.005	8.4
磺胺甲基嘧啶	Sulfamerazine	0.01-1	0.99747	0.01	6.5
磺胺二甲(基)嘧啶	Sulfamethazine	0.001-5	0.99523	0.001	4.4
磺胺甲噻二唑	Sulfamethizole	0.01-10	0.99617	0.01	0.2
磺胺甲基异噁唑	Sulfamethoxazole	0.005-0.5	0.99217	0.005	0.7
磺胺甲氧哒嗪	Sulfamethoxypyridazine	0.01-1	0.99557	0.01	4.2
磺胺	Sulfanilamide	0.05-10	0.99841	0.05	4.3
磺胺苯吡唑	Sulfaphenazole	0.01-1	0.99689	0.01	8.9
磺胺吡啶	Sulfapyridine	0.01-1	0.99684	0.01	8.8
磺胺喹恶啉	Sulfaquinoxaline	0.001-10	0.99461	0.001	8.9
磺胺噻唑	Sulfathiazole	0.01-1	0.99871	0.01	9.5
磺胺二甲异恶唑 (磺胺异噁唑)	Sulfisoxazole	0.001-10	0.99726	0.001	0.4
磺胺醋酰	Sulphacetamide	0.05-10	0.99452	0.05	6.5
舒必利	Sulpiride	0.005-1	0.99508	0.005	5.3
吡螨胺	Tebufenpyrad	0.01-10	0.99051	0.01	4.6
替米沙坦	Telmisartan	0.005-0.5	0.99459	0.005	9.0
替马西泮	Temazepam	0.01-10	0.99491	0.01	5.6
特丁通	Terbumeton	0.001-5	0.9944	0.001	5.8
特丁津-2-羟基	Terbuthylazin 2 hydroxy	0.001-10	0.99749	0.001	0.6
特丁津-脱乙基-2-羟基	Terbuthylazin desethyl 2 hydroxy	0.001-10	0.99908	0.001	1.4
特丁草净	Terbutryn	0.001-5	0.99579	0.001	1.2
特丁津	Terbutylazin	0.001-10	0.99537	0.001	7.4
睾丸酮	Testosterone	0.001-10	0.9981	0.001	2.0
丙酸睾丸素 (丙酸睾酮)	Testosterone propionate	0.01-1	0.99964	0.01	0.7
四环素	Tetracycline	0.05-10	0.99503	0.05	7.0
四环素	Tetracycline	0.01-50	0.99424	0.01	5.7
噻苯咪唑 (噻菌灵)	Thiabendazole	0.001-5	0.9941	0.001	6.4
甲基噻吩磺隆	Thifensulfuron methyl	0.01-10	0.99554	0.01	1.3
替米考星	Tilmicosin	0.01-1	0.99394	0.01	1.7
甲苯磺丁脲	Tolbutamide	0.01-10	0.99424	0.01	3.7
苯唑草酮	Topramezone	0.05-10	0.99672	0.05	6.9
群勃龙; β-群勃龙; 孕三烯酮	Trenbolone	0.01-10	0.9976	0.01	5.2
威菌磷	Triamiphos	0.001-10	0.9956	0.001	5.0
三唑仑	Triazolam	0.001-10	0.99309	0.001	1.6
苯磺隆	Tribenuron methyl	0.001-10	0.99606	0.001	6.6
苯磺隆	Tribenuron methyl	0.005-1	0.99287	0.005	6.2
三氯卡巴 (三氯卡班)	Triclocarban	0.01-10	0.9984	0.01	5.9
三氯森	Triclosan	0.05-100	0.99873	0.05	0.3
氟胺磺隆	Triflusulfuron methyl	0.001-10	0.99934	0.001	8.8
甲氧苄氨嘧啶	Trimethoprim	0.001-1	0.99656	0.001	1.8
缬沙坦	Valsartan	0.01-5	0.99653	0.01	8.4
维吉尼霉素 S1	Virginiamycin S	0.005-100	0.99684	0.005	6.0
维吉尼霉素 M1	Virginiamycins M	0.005-1	0.99243	0.005	3.1
华法令	Warfarin	0.001-1	0.99619	0.001	9.4
唑吡坦	Zolpidem	0.005-1	0.99624	0.005	3.2

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内容提要

SWATH®采集技术应用于水中371种农药及PPCPs的筛查和定量分析

翟南南，贾彦波，靳文海

SCIEX中国

随着我国工农业的迅速发展，近年来水环境的污染问题日渐严重化，水环境的污染主要来自于水体中逐渐增加的一些微量有机污染物，如除草剂、杀虫剂等农药，消毒副产物，药物及个人护理品（PPCPs）等，其去除作用极其有限。同时，由于水体受到污染，导致水体富营养化，藻类过量繁殖，产生难闻的嗅味和有害的藻毒素。对日常饮用水带来了极大的危害，严重影响着人群健康水平。

为使人们能放心的继续享受水资源，如何有效的对水环境中污染物的进行监测显得尤为重要。

本文针对水环境污染物问题，在X500R QTOF系统上建立了371种农药及PPCPs的快速筛查方法，为监测工作者们提供了高效准确的多农残及PPCPs的解决方案。

本方法具有以下特点：

1. 一针进样同时测定371种农药及环境污染物，分析仅时间20分钟，提高工作效率及通量。
2. 一针进样同时实现定性定量。不仅具备一级质量精度、保留时间、化合物同位素丰度、二级谱库匹配四重关卡，还有可满足欧盟最新的法规要求ion ratio，保证筛查结果准确可靠，为农残及环境污染物的快速筛查工作保驾护航。
3. 水样品直接进样，无需富集，简单、快速，省时、省力。

实验思路

1. 建立SWATH®采集方法，一针进样获得高质量一级和二级质谱信息
2. SCIEX OS软件多维度确证样品信息
3. 一级信息同时进行定性定量
4. 二级信息数据库比对及Ion Ratio对阳性化合物确认

仪器设备

SCIEX ExionLC™系统+ X500R QTOF系统

数据采集和处理采用SCIEX OS软件

样品制备

水样样品直接进样分析。

液相方法

流动相A: 水（含5 mM 甲酸铵）流动相B：甲醇（含5 mM 甲酸铵）；色谱柱：Phenomenex Kinetex Biphenyl，100×3.0 mm，2.6 μm。

质谱方法

SWATH数据采集方式，ESI源正离子扫描，一次进样同时采集TOF-MS和MS/MS数据。

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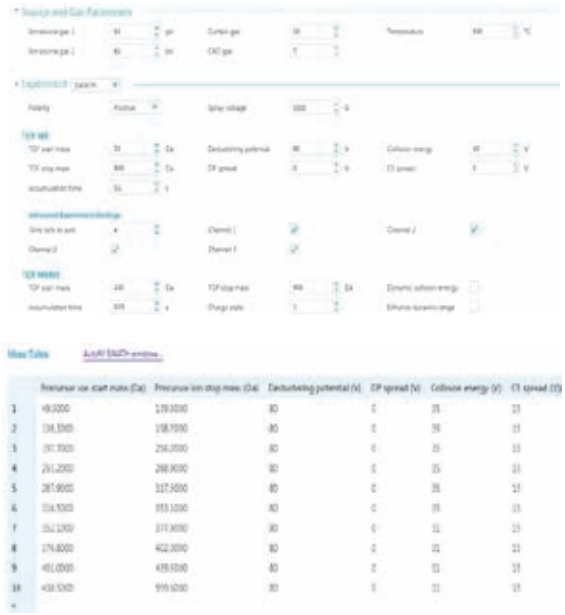
内容提要



实验结果

1. 一次进样同时对371种农药级环境污染物进行筛查，每个农药都有固定的保留时间，在本方法条件下即使在无标准品情况下也可根据保留时间进行筛查。

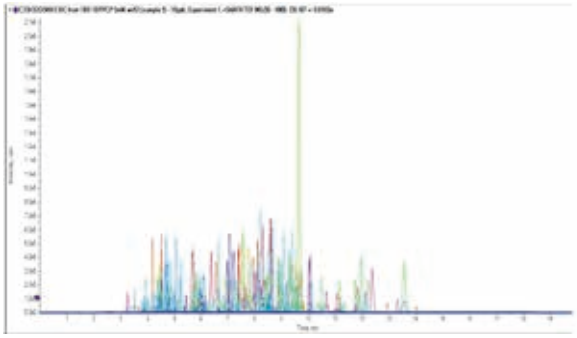
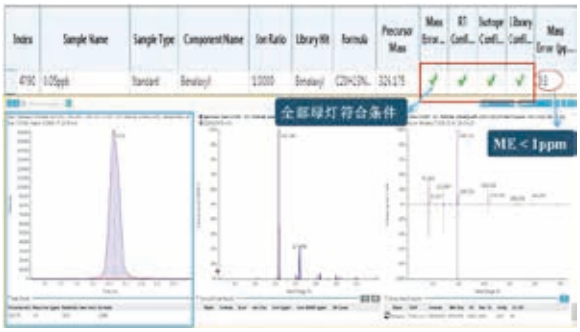


图1. 371种农药及环境污染物提取色谱图（10 ppb）

2. 一针进样，获得全面且高质量的一级和二级质谱信息，可同时定性定量。

SWATH采集技术对化合物母离子的质量范围进行智能窗口划分，每个窗口内的所有离子一起碰碎，从而得到质量范围内所有离子的一级和二级质谱信息，进一步通过软件智能去卷积进行数据库匹配。



色谱图　　同位素分布图　　二级质谱图

图2. SWATH®采集一级定性结果示例图（通过Mass error、RT、Isotope、Library判定筛查结果）

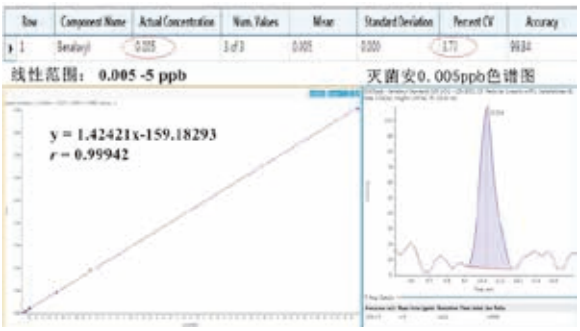


图3. SWATH一级定量结果示例图【灵敏度（0.005ppb）和重现性（以灭菌安为例）】

3. SWATH®采集二级完整的数据库匹配及符合最新欧盟SANTE/11945/2015农残筛查标准要求的Ion Ratio为筛查保驾护航

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内容提要

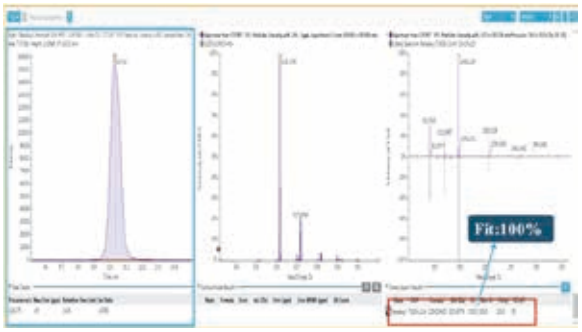

图3. SWATH二级库匹配示例图

欧盟发布的农残鉴定指导文件(SANTE/11945/2015)，要求在使用高分辨质谱进行鉴定时，不仅要求提供高质量精度的一级和二级质谱信息（< 5 ppm），而且规定了两个离子的峰面积ion ratio在样品和标准品中偏差不超过30%。

运用SWATH®采集技术采集样品数据，在数据处理方法编辑界面可智能选择ion ratio限定范围。在结果的展示上以“交通灯”的方式对阳性结果进行判定，满足欧盟农残筛查的法规要求。

4. 可溯源式数据分析，无需再次采集数据

SWATH®采集技术采集样品数据，所有化合物的全部二级碎片都被采集并记录，具有可溯源性。无需重复进样，可根据需求随时调用关注信息，节省实验时间和成本。

5. 样品处理简单

传统的水样前处理一样采用SPE方法进行富集，本方法采用大体积进样方法，简单快速易操作。

图5. SCIEX OS 软件结果列表中ion ratio结果展示

总结

本方法在X500R QTOF系统上，建立了水质中371种农药及环境污染物的SWATH数据采集和数据处理方法。该方法可实现一针进样同时测定371种化合物，在短短20分钟内同时获得所有化合物的一级和二级质谱信息。不仅具备以一级质量精度，保留时间，同位素丰度，二级信息数据库匹配的功能确定阳性样品，还可满足欧盟SANTE/11945/2015农残筛查标准中关于ion ratio 的判定标准，实现真正意义上的一针进样同时定性定量分析，大大提高了工作效率和通量，节省人力物力和财力。

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内容提要

生活饮用水中双酚A类内分泌干扰物残留量的测定

Determination of bisphenol A endocrine disruptors residues in drinking water

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Key Words : Bisphenol A , Drinking Water

引言

双酚A（Bisphenol A，简写作BPA），是工业上用来合成聚碳酸酯、环氧树脂、酚醛树脂等高分子材料的重要单体，广泛应用于制造塑料食品容器，如保鲜盒、婴儿奶瓶和矿泉水瓶等。研究发现双酚A为代表的双酚类化合物（常见的还有双酚B、双酚F和双酚S等）有类似雌激素的作用，即使很低的剂量也有诱发儿童性早熟、导致内分泌失调等危害。由于双酚A的广泛应用，且不易降解，近年来不断有地表水、地下水甚至饮用水中检出双酚A报道，双酚A的水体污染已成为饮用水安全领域的一个重要问题。现行GB 5749-2006，以及2022年3月发布的GB 5749-2022版《生活饮用水卫生标准》，都将双酚A作为饮用水安全的参考指标，限值0.01mg/L。本文参照生活饮用水标准检测方法（征求意见稿）GB/T 5750.8-74.1生活饮用水中双酚A残留量测定方法，建立了包括大体积水样富集净化的前处理方案在内的酚类内分泌干扰物的液质测定方法，待测物包括双酚A、双酚B、双酚F和另外两种烷基酚类内分泌干扰物4-壬基酚和4-辛基酚。

本实验方法具有如下特点：

1、本方法灵敏度可达到飞克级别，满足GB/T 5750.8征求意见稿中5种双酚A类内分泌干扰物的检测需求。

2、方法回收率高、稳定性好：空白基质添加0.5、5、50 μg/L三个浓度，每个添加浓度重复6次，平均回收率在85%-120%间，相对标准偏差小于10%。

化合物信息

表1. 化合物信息

中文名称	英文名称	CAS号	分子式
双酚A	Bisphenol A	80-05-7	$C_{15}H_{16}O_2$
双酚B	Bisphenol B	77-40-7	$C_{16}H_{18}O_2$
双酚F	4,4'-methylene bisphenol	620-92-8	$C_{13}H_{12}O_2$
4-壬基酚	4-Nonylphenol	104-40-5	$C_{15}H_{24}O$
4-辛基酚	4-Octylphenol	1806-26-4	$C_{14}H_{22}O$
4-壬基酚-D_5	4-n-Nonylphenol-D_5	358730-95-7	$C_{15}D_5H_{19}O$

实验部分

3.1仪器、试剂与材料

3.1.1 主要仪器设备

大体积上样固相萃取装置 (Agela MULTI-SPE M08)；

氮吹浓缩仪(Agela Cleanert V96)。

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3.1.2 试剂材料

固相萃取柱：Cleanert PEP-2, 200 mg/6mL, P/N: PE2006-2；

实验用水、甲醇均为色谱级，氨水为分析纯。

3.1.3 样品

纯净水样作为空白样品，备用。

3.1.4 标准品

双酚A、双酚B、双酚F、4-辛基酚、4-壬基酚、4-壬基酚-D_5 (100 mg/L)标准溶液外购，避光-18 ℃保存；

双酚A、双酚B、双酚F、4-辛基酚、4-壬基酚、4-壬基酚-D_5中间溶液(1 mg/L)由原液稀释而成，避光4 ℃保存；

双酚A、双酚B、双酚F、4-辛基酚、4-壬基酚、4-壬基酚-D_5工作溶液(100 μg/L)现用现配。

3.2 样品前处理方法

活化：PEP-2固相萃取柱使用前依次用 5 mL 甲醇、10 mL 水活化；

富集：取备用水样100 mL，加入50 μL 浓度为100 μg/L 4-壬基酚-D_4内标工作液，混匀，内标物在水中浓度为0.050 μg/L，水样以约 5 mL/min 速度通过固相萃取柱。

干燥：用氮气吹2 min，使固相萃取柱干燥；

洗脱：用 15 mL 甲醇分 3 次洗脱，洗脱液下降滴速控制在 1 滴/3 s 左右；

洗脱液浓缩：洗脱液在50 ℃用氮气吹至近干，再用50%甲醇溶液定容至1 mL。

3.3 仪器检测条件

3.3.1 色谱条件

色谱柱： Kinetex EVO C18（2.1×100mm, 1.7 μm, 100Å）；P/N:00D-4726-AN

流动相A相：0.01%氨水水溶液；

流动相B相：甲醇；

流 速：0.3 mL/min；

柱 温：40 ℃；

梯度程序见表2：

表2. 梯度条件

时间 (min)	流速 (mL/min)	A (%)	B (%)
0	0.3	60	40
1.0	0.3	60	40
4.0	0.3	5	95
7.5	0.3	5	95
7.6	0.3	60	40
9.5	0.3	60	40

3.3.2 质谱条件

离子源类型：电喷雾离子源（ESI-）

扫描方式：多反应监测负离子模式（MRM）

喷雾针电压：-4500 V　　离子源温度：500 ℃

加热器（GS1）：50 psi　辅助加热气（GS2）：50 psi

气帘气（CUR）：30 psi　碰撞气（CAD）：8

为获得较好的稳定和灵敏度，各化合物（包括内标）监测离子对的去簇电压（DP）和碰撞电压（CE）等参数均经过系统优化，质谱参数见表3。

表3. 化合物定性、定量离子和质谱分析参数

化合物	Q1	Q3	DP/V	CE/V
BPA	227	212*	-90	-24
	227	133	-90	-31
BPB	241	212*	-83	-24
BPF	199	93*	-90	-28
	199	105	-90	-28
4-OP	205	106*	-70	-24
4-NP	219.2	106.1*	-90	-24
4-NP-D_5	223.1	110	-110	-27

注1：表3中标“*”为定量离子。
注2：双酚B、4-NP和4-OP都只有一对MRM
注3：4-NP-D_5为氘五取代内标，但是有一个氘在酚羟基上，其母离子为[M-D]-

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内容提要

3.4 结果与讨论

3.4.1线性范围

分别吸取BPA、BPB、BPF、4-OP、4-NP的标准工作溶液适量，使用50%甲醇溶液稀释，配制成浓度为0.1 μg/L、0.5 μg/L、1 μg/L、5 μg/L、10 μg/L、50 μg/L（其中内标4-NP-D_4浓度为5 μg/L）的混标线性工作溶液，标准曲线见图1。均得到线性良好R^2≥0.999的线性回归方程，见表4（双酚类采用外标法定量，4-NP、4-OP以4-NP-D_5为内标定量）。

表4. 标准曲线

化合物	线性方程	相关系数
BPA	Y=8948.78958X+1285.67803	0.99964
BPB	Y=14923.66589X+351.00256	0.99956
BPF	Y=3595.76330X+323.85210	0.99918
4-NP	Y=0.17843X+0.00865	0.99945
4-OP	Y=0.22237X+0.00572	0.99938

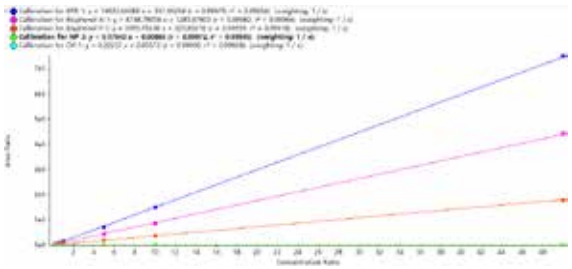

图1. 标准曲线（0.1 μg/L~50 μg/L）

3.4.2方法精密度与准确度

GB 5749-2022《生活饮用水卫生标准》中对双酚A的限量要求不得超过0.01 mg/L，本实验分别选择为0.5、5、50 μg/L三个梯度进行加标测定，每组添加浓度平行测定6次，计算回收率与精密度结果，由表5可得，双酚A各化合物添加浓度的回收率均在85%~120%之内，相对标准偏差RSD小于10%；同位素内标4-NP-D_4回收稳定；实验色谱图见图3/4。

表5. 加标回收实验结果

化合物	理论加标浓度μg/L	平均检测结果μg/L	回收率%	RSD%
BPA	0.5	0.50	100.7%	8.2%
	5	4.94	98.8%	2.7%
	50	48.26	96.5%	2.7%
BPB	0.5	0.45	90.5%	8.2%
	5	4.59	91.8%	5.5%
	50	45.94	91.9%	3.1%
BPF	0.5	0.44	87.8%	9.6%
	5	4.75	95.0%	7.3%
	50	47.73	95.5%	4.0%
4-OP	0.5	0.58	115.7%	4.6%
	5	5.90	118.0%	2.8%
	50	58.36	116.7%	1.3%
4-NP	0.5	0.49	98.7%	6.5%
	5	5.00	100.1%	2.8%
	50	50.70	101.4%	2.4%

3.4.3 讨论

本方法中双酚A、双酚B、双酚F三个化合物直接采用外标法定量回收稳定性良好，满足方法学要求。4-壬基酚、4-辛基酚考虑其化学结构存在较长直碳链结构，过柱富集时与PEP-2结合紧密，在洗脱时存在一定损失，需要增加洗脱体积降低洗脱流速，以4-NP-D_4为内标进行校正定量。

另外，双酚类化合物为合成碳酸酯塑料的原材料，实验过程中应避免污染引入，每批样品分析过程应包括试剂空白、过程空白等质控。本实验试剂空白、过程空白均未检出（见图2），耗材试剂符合要求无本底带入。

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内容提要

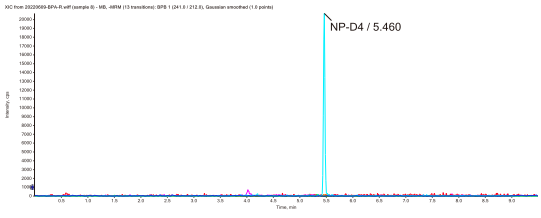

图2. 过程空白总XIC色谱图

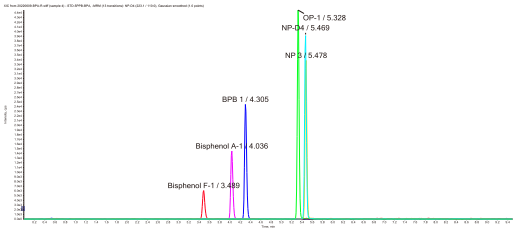

图3. 加标总XIC色谱图

结论

本文重现了GB/T 5750.8-74.1生活饮用水中双酚A等残留量液相色谱-质谱法的测定。使用 MULTI-SPE M08 大体积上样固相萃取装置搭配 Cleanert PEP-2固相萃取小柱对水样进行净化和富集，液相色谱串联质谱同位素内标法检测。实验中线性良好R^2≥0.999，平行性稳定，最低检出限浓度分别为：双酚A、双酚F、4-壬基酚，0.005 μg/L；双酚B、4-辛基酚，0.001 μg/L。各化合物三水平添加回收率在85%~120%之间，RSD值均小于10%，能够满足标准检测方法要求。

3.5实验谱图（见图4）

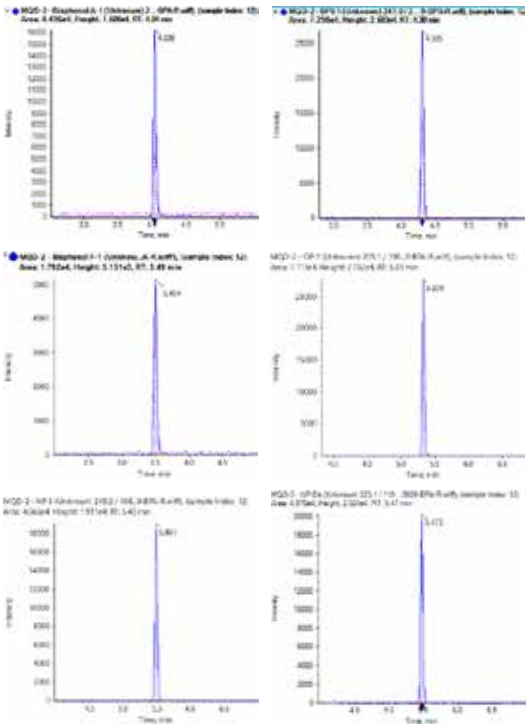

图4. BPA/BPB/BPF/4-OP/4-NP/4-NP-D_5提取色谱图

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内容提要

液相色谱串联质谱法测定纺织品和涂料中的烷基酚聚氧乙烯醚

Determination of Alkylphenol Ethoxylates in Textile and Coatings by LC-MSMS Method

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Key Words: Textile; Coatings; Alkylphenol ethoxylates; Surfactant

1、前言

烷基酚聚氧乙烯醚（APEOs）是一类非离子表面活性剂，其中以壬基酚聚氧乙烯醚（NPEOs）产量最高，约占总产量的80%-85%，其次为辛基酚聚氧乙烯醚（OPEOs），约占15%以上。APEOs的分子结构中同时含有亲水基团和疏水基团，因此，具有良好的如乳化、润湿、渗透性能及起泡、洗涤、去污、抗静电等作用，同时由于其性质稳定、耐酸碱和成本低等特点，广泛应用于纺织工业和内墙涂料生产中。APEOs生物降解缓慢，降解后产生含有较少乙氧基（EO）的APEP和烷基酚（AP），其毒性均远高于母系化合物，能模拟雌性激素作用，危害人体正常的激素分泌，造成“雌性效应”和畸变，并可在生物体内不断累积， 生物链在动物和人体内蓄积，危害巨大，被称为环境激素。

现有的检测标准和方法多用LC和LC-MS方法[1-3]，检测灵敏度、阳性判定和准确度均受限制。因此，建立一套准确测定涂料和纺织品中APEOs残留量的LC-MS/MS方法，具有十分重要的意义。

本文采用了LC-MS/MS法测定了纺织品和水性涂料中残留的OPEOs和NPEOs，采用多反应监测（MRM）的模式，确定了方法的线性范围、回收率和精密度，并对部分涂料和纺织品进行了检测。

本实验优势和特点

多反应监测模式扫描：扫描特异性强，灵敏度高，准确度高，重现性好；

快速高通量：一针进样，7分钟完成辛基酚聚氧乙烯醚（OPEOs）和壬基酚聚氧乙烯醚（NPEOs）的30种同系物的准确定性和定量；

回收率和重现性好：三个不同浓度下的多份添加质控样本的回收率为84-112%，RSD在1.3-4.3%范围内。

2、实验部分

2.1样品前处理

2.1.1涂料的前处理

称取涂料1.0 g，置于50 mL 棕色容量瓶中，用甲醇定容至刻度，再将容量瓶转移至超声中，室温条件下萃取30 min，试样用0.22 μm滤膜过滤，待上机测定[2]。

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2.1.2纺织品的前处理

取5-10 g样品，剪碎至0.5 cm × 0.5 cm以下大小，混匀后，准确称取1.0 g于60 mL样品处理瓶中，加入20 mL甲醇，65 ℃超声萃取30 min；将萃取液移至50 ml容量瓶中，剩余残渣按照上述方法用20、10 mL甲醇再分别萃取2次，萃取液转移至50 mL容量瓶中，定容，取约1 mL上述溶液过0.22 μm滤膜，待上机测定[3]。

2.2 液相方法

色谱柱：Phenomenex C18, 2.6 μm, 2.1 mm × 100 mm

流动相：A：水（5mmol/L乙酸铵）
B：甲醇:乙腈:异丙醇=1:1:1

流速：0.6mL/min

进样量：2 μL

梯度洗脱程序：如表1所示

表1. 液相梯度设置

Time/min	A/%	B/%
0.00	80	20
0.30	80	20
1.00	5	95
4.00	5	95
4.10	80	20
7.00	80	20

2.3质谱方法

扫描方式：MRM采集模式，正离子扫描

离子源：ESI源

离子源参数：

IS电压: 5500 V　　源温度 TEM: 550℃

气帘气 CUR: 30 psi　　碰撞气 CAD: Medium

雾化气 GS1: 55 psi　　辅助气 GS2: 60 psi

离子对参数如表2所示

表2. 化合物离子对参数

化合物名称	母离子	子离子	驻留时间（msec）	ID	去簇电压	碰撞能量
OP2EO	312.2	183.5	8	OP2EO-1	60	17
	312.2	113.3	8	OP2EO-2	60	25
OP3EO	356	227.3	8	OP3EO-1	60	18
	356	165.5	8	OP3EO-2	60	25
OP4EO	400.5	383.4	8	OP4EO-1	80	15
	400.5	271.2	8	OP4EO-2	80	21
OP5EO	444.5	427.6	8	OP5EO-1	80	16
	444.5	315.3	8	OP5EO-2	80	24
OP6EO	488.6	471.5	8	OP6EO-1	100	20
	488.6	359.2	8	OP6EO-2	100	24
OP7EO	532.5	515.4	8	OP7EO-1	120	21
	532.5	133.1	8	OP7EO-2	120	30
OP8EO	576.4	559.5	8	OP8EO-1	120	23
	576.4	447.3	8	OP8EO-2	120	27
OP9EO	620.6	603.5	8	OP9EO-1	120	24
	620.6	277.2	8	OP9EO-2	120	34
OP10EO	664.5	647.5	8	OP10EO-1	120	27
	664.5	277.2	8	OP10EO-2	120	37
OP11EO	708.4	691.5	8	OP11EO-1	120	27
	708.4	277.2	8	OP11EO-2	120	39
OP12EO	752.6	735.6	8	OP12EO-1	120	27
	752.6	277.2	8	OP12EO-2	120	38
OP12EO	796.4	779.6	8	OP13EO-1	100	29
	796.4	277.2	8	OP13EO-2	100	42
OP14EO	840.6	823.6	8	OP14EO-1	120	30
	840.6	277.2	8	OP14EO-2	120	42
OP15EO	884.5	867.6	8	OP15EO-1	100	31
	884.5	277.2	8	OP15EO-2	100	44
OP16EO	928.7	911.7	8	OP16EO-1	80	35
	928.7	277.2	8	OP16EO-2	80	44
NP2EO	326.3	183	8	NP2EO-1	48	15
	326.3	127.3	8	NP2EO-2	48	18
NP3EO	370.3	353.3	8	NP3EO-1	60	12
	370.3	227.1	8	NP3EO-2	60	19
NP4EO	414.4	397.4	8	NP4EO-1	60	15
	414.4	271.1	8	NP4EO-2	60	22
NP5EO	458.4	441.5	8	NP5EO-1	100	20
	458.4	315.3	8	NP5EO-2	100	23
NP6EO	502.4	485.5	8	NP6EO-1	100	21
	502.4	359.3	8	NP6EO-2	100	27
NP7EO	546.4	529.5	8	NP7EO-1	80	23
	546.4	291.2	8	NP7EO-2	80	33
NP8EO	590.5	573.5	8	NP8EO-1	80	25
	590.5	291.2	8	NP8EO-2	80	35
NP9EO	634.4	617.5	8	NP9EO-1	120	27
	634.4	291.2	8	NP9EO-2	120	37
NP10EO	678.4	661.5	8	NP10EO-1	100	27
	678.4	291.2	8	NP10EO-2	100	38

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表2. 化合物离子对参数（续）

化合物名称	母离子	子离子	驻留时间（msec）	ID	去簇电压	碰撞能量
NP11EO	722.4	705.5	8	NP11EO-1	100	29
	722.4	291.2	8	NP11EO-2	100	40
NP12EO	766.4	335.3	8	NP12EO-1	70	36
	766.4	291.4	8	NP12EO-2	70	40
NP13EO	810.6	793.5	8	NP13EO-1	45	32
	810.6	291.4	8	NP13EO-2	45	46
NP14EO	854.7	837.6	8	NP14EO-1	50	33
	854.7	291.3	8	NP14EO-2	50	46
NP15EO	898.7	881.4	8	NP15EO-1	40	33
	898.7	291.3	8	NP15EO-2	40	50
NP16EO	942.6	925.6	8	NP16EO-1	30	36
	942.6	291.2	8	NP16EO-2	30	49

3. 结果与讨论

3.1. 质谱条件的确定

3.1.1 一级质谱条件的确定

0PEOs和NPEOs使用正离子模式，在Q1 MS扫描模式下，主要以［M+NH_4］$^+$、［M+Na］$^+$离子形式存在，表现为m/z为［M+18］$^+$、［M+23］$^+$。烷基酚聚氧乙烯醚，相邻离子之间间隔1个乙氧基（EO：C_2H_4O），相对分子质量相差44；所以OPEOs分子离子主要分布为m/z（224+44n_{EO}）（n_{EO}=2-16），NPEOs分子离子主要分布为m/z（238+44n_{EO}）（n_{EO}=2-16）。由图1可以看出，OPEOs的分子离子中最强的m/z 620.42、664.53和708.58，对应乙氧基链的长度为9、10 和11，NPEOs的分子离子中最强的m/z 634.62、78.73和722.74，对应乙氧基链的长度为9、10 和11，相邻离子之间间隔1个乙氧基（EO:C_2H_4O），相对分子质量相差44，表明该系统条件下不同聚合度的OPEOs和NPEOs均有较好的响应，并呈正态分布。从得到的结果图中可看出OPEOs和NPEOs的［M+NH_4］$^+$的准分子离子峰响应较强，因此选用［M+NH_4］$^+$为化合物的母离子。

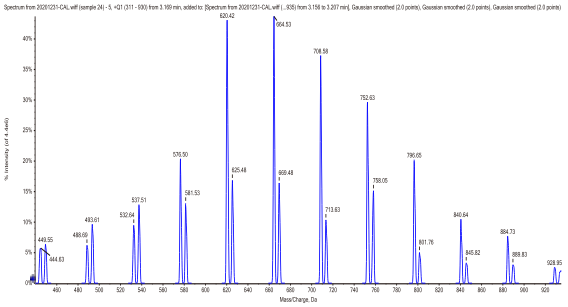

图1. OPEOs的一级全扫描图谱

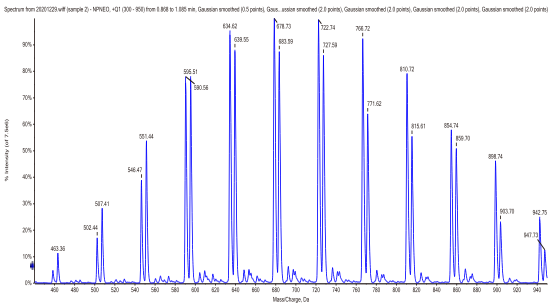

图2. NPEOs的一级全扫描图谱

3.1.2 二级质谱条件的确定

根据聚合物的结构特点，不同聚体的化合物具有相同的碎片组成结构。经化合物结构解析， OPEOs化合物中有典型的结构碎片$C_{18}H_{29}O_2$，如图3所示，m/z为277.2，因此，提取m/z 277.2为子离子，选择母离子扫描模式，得到如图4所示结果，与推测结果完全一致，得到了OPEOs系列化合物的母离子信息。同样方式，NPEOs的典型结构碎片为$C_{19}H_{31}O_2$，如图5所示，m/z为291.2，提取291.2为子离子，选择母离子扫描模式，得到如图6所示结果，与推测结构完全一致，得到了NPEOs同系物的母离子信息。根据此规律，优化得到OPEOs和NPEOs的系列化合物的母离子、子离子、去簇电压和碰撞能量的二级质谱条件，如表2所示。

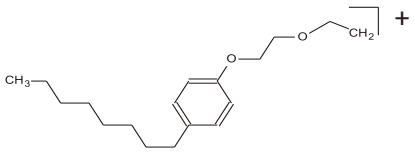

图3. OPEOs碎片$C_{18}H_{29}O_2$结构式， m/z 277.2

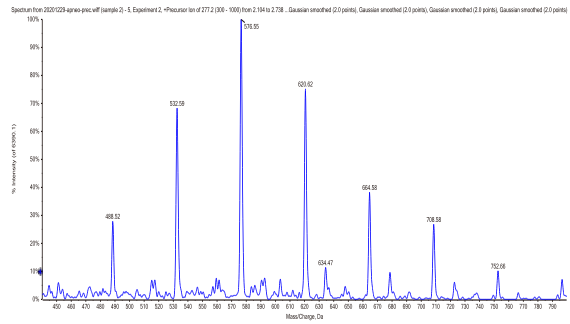

图4. OPEOs化合物母离子扫描结果图， 提取子离子m/z 277.2

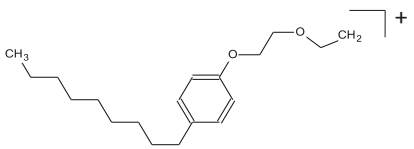

图5. NPEOs碎片$C_{19}H_{31}O_2$结构式，m/z 291.2

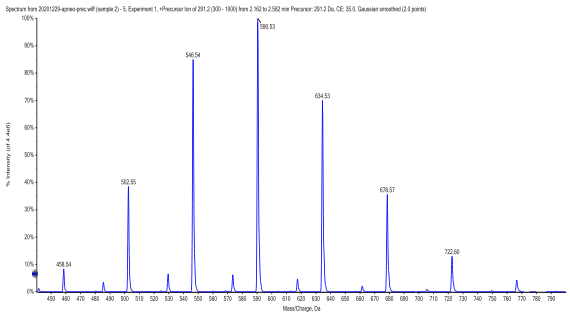

图6. NPEOs化合物母离子扫描结果图， 提取子离子m/z 291.2

3.2. OPEOs和NPEOs化合物的提取离子流图，如图7所示，OPEOs和NPEOs有很好的峰形，同系物中不同的聚合程度有保留时间的差异。

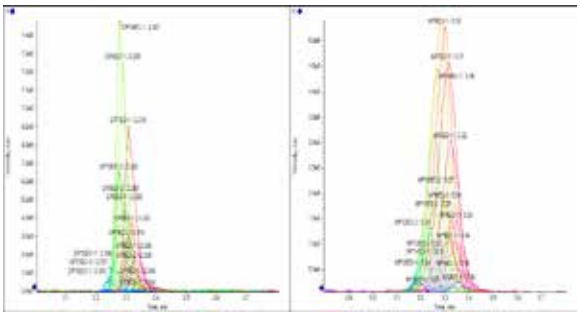

图7. OPEOs和NPEOs的提取离子流图

3.3. 方法线性

该方法中，OPEOs和NPEOs的线性关系良好，相关系数R均大于0.995，保证了不同浓度样品的定量准确性。

3.4. 试剂样本前处理回收率和重复性

称取1.0g的试样，采用超声萃取的前处理方式，分别添加三个浓度水平，每水平6 个平行样，按照仪器条件进行测定。结果表明，不同基质分析方法的回收率为84-112%，相对标准偏差RSD为1.3-4.3%，说明该方法通用性强，完全可以满足日常水性涂料和纺织品中的OPEOs和NPEOs检测的要求。

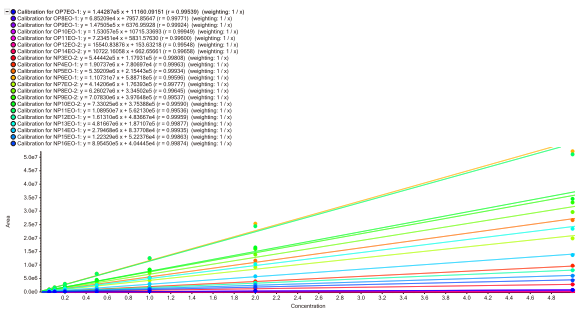

图8. OPEPs和NPEOs的线性结果图

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3.5. 实际样品的测定

采用本方法对市场采购的涂料和纺织品进行检测，结果如表3所示：

表3. 不同涂料和纺织品的检测结果

编号	样品名	OPEOs(mg/kg)	NPEOs(mg/kg)
1	高级环保乳胶漆	-	70.5
2	苯丙乳液	11.2	59.1
3	PU制品	-	114.3
4	天然纤维	-	95.9

4 结论

本文采用SCIEX 液相色谱串联三重四极杆质谱系统，建立了涂料和纺织品中的烷基聚氧乙烯醚的LC-MS/MS检测方法；一针进样，7分钟完成了辛基酚聚氧乙烯醚（OPEOs）和壬基酚聚氧乙烯醚（NPEOs）的测定；本实验验证了实际样品在三个浓度范围的添加回收率，结果均在84-112%，相对标准偏差为1.3-4.3%。该方法快速、准确、全面的完成了涂料和纺织品中的烷基聚氧乙烯醚的测定。

SCIEX液相色谱串联质谱系统优良的仪器性能，保证了实验的高灵敏度、高稳定性和数据的高准确性。

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