SN

中华人民共和国出入境检验检疫行业标准

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出口食品中邻苯二甲酸酯的测定

Determination of phthalate esters(PAEs) in food for export

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前　言

本标准根据 GB/T 1.1—2009《标准化工作导则　第 1 部分：标准的结构和编写》的要求进行编制。

请注意本文件的某些内容可能涉及专利，本文件的发布机构不承担识别这些专利的责任。

本标准由国家认证认可监督管理委员会提出并归口。

本标准起草单位：厦门出入境检验检疫局检验检疫技术中心、深圳出入境检验检疫局、福建省产品质量检验研究院、江西出入境检验检疫局。

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出口食品中邻苯二甲酸酯的测定

第一法　气相色谱-质谱法(GC-MS)

1　范围

本标准规定了食品中23种邻苯二甲酸酯(PAEs)的气相色谱-质谱检测方法。

本标准适用于液体饮料、固体饮料、果酱、果浆、果冻、调味品、香精香料、油脂类食品、乳制品、面淀粉制品及糕点中邻苯二甲酸二甲酯(DMP)、邻苯二甲酸二乙酯(DEP)、邻苯二甲酸二异丙酯(DIPrP)、邻苯二甲酸二烯丙酯(DAP)、邻苯二甲酸二丙酯(DPrP)、邻苯二甲酸二异丁酯(DIBP)、邻苯二甲酸二丁酯(DBP)、邻苯二甲酸二(2-甲氧基)乙酯(DMEP)、邻苯二甲酸二异戊酯(DIPP)、邻苯二甲酸二(4-甲基-2-戊基)酯(BMPP)、邻苯二甲酸二(2-乙氧基)乙酯(DEEP)、邻苯二甲酸二戊酯(DPP)、邻苯二甲酸二己酯(DHXP)、邻苯二甲酸丁基苄基酯(BBP)、邻苯二甲酸二(2-丁氧基)乙酯(DBEP)、邻苯二甲酸二环己酯(DCHP)、邻苯二甲酸二(2-乙基)己酯(DEHP)、邻苯二甲酸二庚酯(DHP)、邻苯二甲酸二苯酯(二苯酯、DPhP)、邻苯二甲酸二正辛酯(DNOP)、邻苯二甲酸二异壬酯(DINP)、邻苯二甲酸二异癸酯(DIDP)、邻苯二甲酸二壬酯(DNP)(见表A.1)测定和确证。

2　方法提要

各类食品提取、净化后经气相色谱-质谱联用仪进行测定。采用特征选择离子监测扫描模式(SIM),以色谱保留时间和碎片的丰度比定性,以标准样品定量离子的峰面积外标法定量。

3　试剂和材料

除特殊注明外,所有试剂均为分析纯(储存于玻璃瓶中,避免接触塑料),水为去离子水。

3.1　正己烷:色谱纯。

3.2　乙腈:色谱纯。

3.3　甲醇:色谱纯。

3.4　丙酮:色谱纯。

3.5　氯化钠。

3.6　硫酸镁:色谱纯。

3.7　醋酸钠:色谱纯。

3.8　PSA粉:粒径为40 μm或120 μm,孔径为60 Å。

3.9　C_{18}粉:粒径为40 μm或120 μm,孔径为60 Å。

3.10　SPE小柱:ProElut PSA玻璃柱(1 g,6 mL),使用前,加入5 mL丙酮和5 mL正己烷进行活化。

3.11　标准品:详细信息见表A.1。

3.12　标准储备液:分别称取适量上述各种标准品(精确至0.1 mg),用正己烷配制成1 000 mg/L的储备液,于4 ℃冰箱中避光保存。

3.13　标准使用液:将标准储备液用正己烷稀释至浓度为0.1 mg/L,0.5 mg/L,1.0 mg/L,2.0 mg/L,5.0 mg/L,10.0 mg/L的标准系列溶液待用。

4 仪器和设备

4.1 气相色谱-质谱联用仪(GC-MS),配电子轰击离子源(EI)。
4.2 分析天平:感量 0.1 mg 和 0.01 g。
4.3 离心机:不低于 4 000 r/min。
4.4 氮吹仪。
4.5 振荡器。
4.6 涡旋混合器。
4.7 高速均质器:18 000 r/min。
4.8 超声提取器。
4.9 组织捣碎机。
4.10 冷冻离心机:不低于 4 000 r/min。

5 试样制备、保存

5.1 试样制备

5.1.1 固体、半固体、液体样品

至少取同一批次 3 个最小完整包装样品(混合后的固体样品总量 100 g～500 g,液体样品 100 mL～500 mL),置于硬质全玻璃器皿中,固体或半固体样品粉碎混匀,液体样品混合均匀,待称样处理。

5.1.2 胶囊、锭状或粉状样品

取有代表性样品 500 g(胶囊取内含物),采用粉碎机粉碎后,再将其研磨成细粉状,装入洁净的玻璃盛样容器内,密封并标明标记。

5.2 试样保存

粉状试样于 0 ℃～4 ℃保存;其他试样于－18 ℃以下冷冻保存。在制样的操作过程中,避免接触塑料,应防止样品受到污染或发生被测物含量的变化。

6 测定步骤

6.1 试样处理

6.1.1 液体试样

6.1.1.1 不易乳化液体样

准确称取混合均匀的液体试样 5.0 g(精确到 0.01 g)(含有二氧化碳气体的先除去二氧化碳)于 25 mL 具塞磨口玻璃试管中,加入氯化钠至水相饱和,加入 5.0 mL 正己烷,涡旋 1 min,4 000 r/min 离心 2 min,收集上清液,供 GC-MS 分析。

6.1.1.2 易乳化液体样

准确称取混合均匀的液体试样 5.0 g(精确到 0.01 g)(含有二氧化碳气体的先除去二氧化碳)于 25 mL 具塞磨口玻璃试管中,加 10 mL 乙腈,涡旋 1 min,4 000 r/min 离心 2 min,取上清液到一洁净的

25 mL 玻璃离心管中，加入氯化钠至水相饱和，涡旋 1 min，静置或离心分层，取上层（乙腈层）到另一洁净玻璃管中，吹氮浓缩至近干后挥干，用正己烷定容至 5 mL，供 GC-MS 分析。

6.1.2 不含油脂固体或半固体试样

准确称取混合均匀固体或半固体试样 5.0 g（精确到 0.01 g）于 50 mL 具塞磨口玻璃试管中，加水 10 mL（视试样水分含量，可适当增加加水量），加入氯化钠至水相饱和，加入 10.0 mL 乙腈，涡旋 1 min，超声提取 20 min，4 000 r/min 离心 2 min，收集上清液。重复提取一次，合并上清液。将提取液于 40 ℃氮吹至近干后挥干，用正己烷定容至 5 mL，供 GC-MS 分析。

6.1.3 含油脂试样

准确称取混合均匀试样 1.0 g（精确到 0.01 g）于 25 mL 具塞磨口玻璃试管中，加入 5 mL 乙腈，涡旋 1 min，4 000 r/min 离心 2 min，收集上清液。重复提取一次，合并上清液。将提取液于 40 ℃氮吹至近干，用甲醇定容至 1 mL，放入－18 ℃的冰箱冷藏 2h，4 000 r/min 4℃冷冻离心 2 min，取上清液，供 GC-MS 分析。

6.1.4 QuEChERS 法

6.1.2 和 6.1.3 试样也可采用如下方法：准确称取混合均匀固体或半固体试样 5.0 g（精确到 0.01 g）于 50 mL 具塞磨口玻璃试管中，加入 5 mL 水（含水试样，无需加水），准确加入 15 mL 乙腈，加入 6 g $MgSO_4$ 和 1.5 g 醋酸钠，涡旋 1 min，4 000 r/min 离心 2 min，收集上清液，于 40 ℃氮吹至近干。用乙腈定容至 5 mL，加入 50 mg PSA 粉（3.8），50 mg C_{18} 粉（3.9），150 mg $MgSO_4$，涡旋 1 min，4 000 r/min 离心 2 min，取上清液，供 GC-MS 分析。

6.1.5 SPE 法

6.1.2 和 6.1.3 试样还可采用如下方法：准确称取样品 1.0 g 于玻璃离心管中，加入 2 mL 正己烷和 10 mL 乙腈，涡旋混合 2 min，4 000 r/min 离心 2 min，分层，取出下层清液。以 10 mL 乙腈重复提取样品一次，合并两次提取液，40 ℃下氮气吹至近干，加入 2 mL 正己烷，振荡混匀（待净化液）。把待净化液加入 SPE 小柱（3.10），流速控制在 1 mL/min 内，收集流出液；再依次加入 5 mL 正己烷、5 mL 4%丙酮-正己烷溶液，收集流出液，合并两次收集的流出液，40 ℃氮气吹至近干后挥干，正己烷定容至 1 mL，供 GC-MS 分析。

6.2 测定

6.2.1 气相色谱-质谱条件

气相色谱-质谱条件如下：

a) 色谱柱：TG/DB-5MS 石英毛细管柱，60 m×0.25 mm（内径），0.25 μm（膜厚），或相当者；
b) 进样口温度：280 ℃；
c) 载气为 99.999% He 气，恒流模式，流速为 1.5 mL/min；
d) 离子源温度：250 ℃；
e) 电离能量：70 eV；
f) 接口（传输线）温度：300 ℃；
g) 电子轰击电离源（EI），选择离子监测模式（SIM），特征离子参见表 B.1，分组监测见表 1；
h) 溶剂延迟时间：10 min；
i) 进样量：1.0 μL；

j) 进样方式:不分流进样。

表 1 选择离子监测分组表

通 道	时间/min	选择离子(m/z)
1	10.5	77,135,163,194
2	12.4	149,177,121,222
3	14.5	149,167,209
4	16.2	104,132,149,189
5	17.7	76,149, 191,209
6	19.1	149,167,205,223
7	21.5	121,149,223,205
8	23.2	59,104,149, 207
9	24.7	69,85,104,149,167,251
10	26.4	72,149,176,193
11	27.4	104,149,219,237
12	30.1	76,91,149,104,206,251
13	33.7	85,101,149,193
14	35.4	104,149,167,247,249,265,279
15	36.4	77,104,153,225
16	38.7	149,167,261,279
17	40.9	85,127,141,149,167,261,279,293,307

6.2.2 色谱分离条件

可以较好地分离目标分析物的升温程序见表 2。

表 2 GC-MS 方法程序升温

	升温速率 ℃/min	温度 ℃	保持时间 min
初始	—	60	1.00
阶段 1	30.0	160	1.00
阶段 2	3.5	220	2.00
阶段 3	5.0	270	5.00
阶段 4	2.0	280	7.00
阶段 5	10.0	300	1.00

6.2.3 气相色谱-质谱法测定

根据样液中被测物含量情况,选定浓度相近的标准工作溶液,对标准工作溶液、样液及空白试验溶液等体积参插进样测定,标准工作溶液和待测样液中每种邻苯二甲酸酯的响应值均应在仪器检测的线性范围内。在上述气相色谱-质谱条件下,23 种邻苯二甲酸酯化合物的参考保留时间参见表 B.1,气相

色谱-质谱选择离子色谱图参见图 C.1。如果样液保留时间与标准溶液相一致(±0.5%),并且在扣除背景后的样品质谱图中,所选择的离子均出现,而且所选择的离子峰度比与标准样品的离子峰度比相一致,则可判断样品中存在这种被测物。使用气相色谱-质谱定性分析时,相对离子丰度最大允许误差见表 3。

表 3 定性时相对离子丰度的最大允许偏差

相对离子丰度	>50%	>20%～50%	>10%～20%	≤10%
允许的相对偏差	±10%	±15%	±20%	±50%

6.3 空白实验

除不加试样外,均按上述测定步骤进行。

7 质量控制

7.1 取样制样

取样制样均应采用不锈钢或玻璃器具,避免接触塑料。

7.2 有机溶剂

本标准中使用到的所有有机溶剂,在使用前,应进行空白实验。如本底值高于定量限,应对有机溶剂进行重蒸,直至本底值低于定量限。

7.3 玻璃器皿

所用玻璃器皿洗净后,用去离子水淋洗三次,于丙酮浸泡 1 h,在 200℃下烘干 2 h,冷却至室温备用。

8 结果计算和表述

用色谱数据处理机或按式(1)分别计算试样中被测化合物的含量,计算结果应扣除空白值。

$$X_i = \frac{A_i \times c_i \times V}{A_{is} \times m} \quad \cdots\cdots (1)$$

式中:

X_i ——试样中每种被测化合物含量,单位为毫克每千克(mg/kg);

A_i ——样液中每种被测化合物的峰面积;

c_i ——标准工作液中每种化合物的浓度,单位为微克每毫升(μg/mL);

V ——样液最终定容体积,单位为毫升(mL);

A_{is}——标准工作液中每种化合物的峰面积;

m ——最终样液代表的试样质量,单位为克(g)。

9 方法定量限、回收率

9.1 定量限

本方法的定量限(LOQ)DINP、DIDP 为 0.5 mg/kg,其他化合物为 0.1 mg/kg。

9.2 回收率

分别在番石榴汁、固体乳酸菌饮料、调味精粉、葡萄果冻、柠檬香精、水果酥、柚子酱、鸡蛋面、食用橄榄油、木瓜牛奶中添加23种邻苯二甲酸酯，添加浓度及其回收率数据参见表D.1。

第二法 液相色谱-质谱/质谱法(LC-MS/MS)

10 范围

本标准规定了食品中23种邻苯二甲酸酯(PAEs)的液相色谱串联质谱检测方法。

本标准适用于液体饮料、固体饮料、果酱、果浆、果冻、调味品、香精香料、油脂类食品、乳制品、面淀粉制品及糕点中邻苯二甲酸二甲酯(DMP)、邻苯二甲酸二乙酯(DEP)、邻苯二甲酸二异丙酯(DIPrP)、邻苯二甲酸二烯丙酯(DAP)、邻苯二甲酸二丙酯(DPrP)、邻苯二甲酸二异丁酯(DIBP)、邻苯二甲酸二丁酯(DBP)、邻苯二甲酸二(2-甲氧基)乙酯(DMEP)、邻苯二甲酸二异戊酯(DIPP)、邻苯二甲酸二(4-甲基-2-戊基)酯(BMPP)、邻苯二甲酸二(2-乙氧基)乙酯(DEEP)、邻苯二甲酸二戊酯(DPP)、邻苯二甲酸二己酯(DHXP)、邻苯二甲酸丁基苄基酯(BBP)、邻苯二甲酸二(2-丁氧基)乙酯(DBEP)、邻苯二甲酸二环己酯(DCHP)、邻苯二甲酸二(2-乙基)己酯(DEHP)、邻苯二甲酸二庚酯(DHP)、邻苯二甲酸二苯酯(二苯酯、DPhP)、邻苯二甲酸二正辛酯(DNOP)、邻苯二甲酸二异壬酯(DINP)、邻苯二甲酸二异癸酯(DIDP)、邻苯二甲酸二壬酯(DNP)(见表A.1)测定和确证。

11 方法提要

本方法用乙腈对样品中的邻苯二甲酸酯进行提取，LC-MS/MS测定和确证，外标法定量。

12 试剂和材料

除特殊注明外，所有试剂均为分析纯，水为去离子水。

12.1 甲醇：色谱纯。

12.2 乙腈：色谱纯。

12.3 正己烷：色谱纯。

12.4 丙酮：色谱纯。

12.5 氯化钠。

12.6 硫酸镁：色谱纯。

12.7 醋酸钠：色谱纯。

12.8 PSA粉：同3.8。

12.9 C_{18}粉：同3.9。

12.10 SPE小柱：同3.10。

12.11 甲酸。

12.12 0.1%甲酸水溶液：量取1 mL甲酸和999 mL水混匀，备用。

12.13 邻苯二甲酸酯标准品：同3.11。

12.14 标准储备溶液：分别准确称取适量的23种PAEs标准品于100 mL容量瓶中，用甲醇配制成质量浓度为100 μg/mL的标准储备液。

12.15 标准工作溶液：根据需要再用甲醇逐级稀释成适用浓度的系列混合标准工作溶液。线性范围：

0.01 mg/L～1 mg/L。

13 仪器和设备

13.1 液相色谱串联质谱，配电喷雾离子源(ESI)。
13.2 分析天平：感量 0.1 mg 和 0.01 g。
13.3 离心机：不低于 4 000 r/min。
13.4 高速均质器：18 000 r/min。
13.5 超声提取器。
13.6 振荡器。
13.7 氮吹仪。
13.8 涡旋混合器。
13.9 组织捣碎机。
13.10 冷冻离心机：不低于 4 000 r/min。

14 试样制备与保存

14.1 试样制备

同 5.1。

14.2 试样保存

同 5.2。

15 测定步骤

15.1 试样处理

15.1.1 液体试样

15.1.1.1 不易乳化液体样

准确称取混合均匀的液体试样 5.0 g(精确到 0.01 g)(含有二氧化碳气体的先除去二氧化碳)于 25 mL 具塞磨口玻璃试管中，加入固体氯化钠至水相饱和，加入 5.0 mL 乙腈，涡旋 1 min，4 000 r/min 离心 2 min，收集上清液，供 LC-MS/MS 分析。

15.1.1.2 易乳化液体样

准确称取混合均匀的液体试样 5.0 g(精确到 0.01 g)(含有二氧化碳气体的先除去二氧化碳)于 25 mL 具塞磨口玻璃试管中，加 10 mL 乙腈，涡旋 1 min，4 000 r/min 离心 2 min，分取上清液到一洁净的 25 mL 玻璃离心管中，加入固体氯化钠至水相饱和，涡旋 1 min，静置或离心分层，取上层(乙腈层)到另一洁净玻璃管中，吹氮浓缩至近干，用乙腈定容为 5 mL，供 LC-MS/MS 分析。

15.1.2 不含油脂固体或半固体试样

同 6.1.2。仅吹至近干，用乙腈定容至 5 mL，供 LC-MS/MS 分析。

15.1.3 含油脂固体或半固体试样

同6.1.3，供LC-MS/MS分析。

15.1.4 QuEChERS法

15.1.2和15.1.3的试样也可采用如下方法：同6.1.4，供LC-MS/MS分析。

15.1.5 SPE法

15.1.2和15.1.3的试样还可采用如下方法：同6.1.5，仅吹至近干后挥干，用乙腈定容至1 mL，供LC-MS/MS分析。

15.2 测定

15.2.1 液相条件

液相条件如下：

a) 色谱柱Ⅰ：Poroshell 120 EC-C_{18}柱，100 mm×4.6 mm(内径)，2.7 μm；色谱柱Ⅱ：Accucore RP-MS柱，100 mm×2.1 mm(内径)，2.6 μm；或相当者；

b) 流动相：甲醇-0.1%甲酸溶液，梯度洗脱见表4；

c) 流速：见表4；

d) 柱温：35 ℃；

e) 进样量：10 μL。

表4 液相色谱的梯度洗脱条件

时间/min	A 0.1%甲酸水溶液/%	B甲醇/%	流速/(mL/min)
Poroshell 120 EC-C_{18}柱，100 mm×4.6 mm(内径)，2.7 μm			
0	30	70	0.7
4.0	5	95	0.7
6.0	5	95	0.7
6.1	0	100	0.7
11.0	0	100	0.7
11.1	30	70	0.7
15.0	30	70	0.7
Accucore RP-MS柱，100 mm×2.1 mm(内径)，2.6 μm			
0	60	40	0.3
12.0	0	100	0.3
15.0	0	100	0.3
15.1	60	40	0.3
18.0	60	40	0.3

15.2.2 质谱条件

质谱条件如下：

a) 离子化模式：电喷雾电离正离子模式(ESI^+)；

b) 质谱扫描方式：多反应监测(MRM)；

c) 分辨率：单位质量分辨率；

d) 其他参考质谱条件参见 B.2。

15.2.3 液相色谱串联质谱测定

根据试样中被测物的含量，选取响应值适宜的标准工作溶液进行分析。对标准工作溶液、样液及空白试验溶液等体积参插进样测定。标准工作液和待测样液中 23 种邻苯二甲酸酯化合物的响应值均应在仪器线性响应范围内。如果含量超过标准曲线范围，应稀释到合适浓度后分析。在上述 LC-MS/MS 条件下，23 种邻苯二甲酸酯化合物的参考保留时间参见表 B.2。邻苯二甲酸酯化合物标准品 MRM 图参见附录 C 中图 C.2 和 C.3。在相同的实验条件下，样液中被测物的色谱峰保留时间与标准工作液相同，并且在扣除背景后的样液谱图中，所选择的离子对均出现，各定性离子的相对丰度与标准品离子的相对丰度相比，误差不超过表 5 规定的范围内，则可判断样品中存在对应的被测物。

表 5 定性确证时相对离子丰度的最大允许误差

相对离子丰度	＞50%	＞20%～50%	＞10%～20%	≤10%
允许的相对偏差	±20%	±25%	±30%	±50%

15.3 空白实验

除不加试样外，均按上述测定步骤进行。

16 质量控制

同第 7 章。

17 结果计算和表述

用色谱数据处理机或按式(2)分别计算试样中被测化合物的含量，计算结果应扣除空白值。

$$X=\frac{A\times c_s\times V}{A_s\times m} \qquad \cdots\cdots(2)$$

式中：

X ——试样中每种被测化合物的含量，单位为毫克每千克(mg/kg)；

A ——样液中每种被测化合物的峰面积；

c_s ——标准工作液中每种化合物的浓度，单位为微克每毫升(μg/mL)；

V ——样液最终定容体积，毫升(mL)；

A_s——标准工作液中每种化合物的峰面积；

m ——最终样液所代表的试样量，单位为克(g)。

18 方法定量限、回收率

18.1 定量限

本方法的定量限(LOQ)DAP 为 0.01 mg/kg，其他化合物为 0.1 mg/kg。

18.2 回收率

分别在番石榴汁、固体乳酸菌饮料、调味精粉、葡萄果冻、柠檬香精、水果酥、柚子酱、鸡蛋面、食用橄榄油、木瓜牛奶中添加23种邻苯二甲酸酯，添加浓度及其回收率数据参见表D.2。

附 录 A
（规范性附录）
邻苯二甲酸酯化合物信息

表 A.1 23种邻苯二甲酸酯化合物信息

序号	中文名称	英文名称	缩写	CAS号	分子式	含量/%≥
1	邻苯二甲酸二甲酯	Dimethyl phthalate	DMP	131-11-3	$C_{10}H_{10}O_4$	99.5
2	邻苯二甲酸二乙酯	Diethyl phthalate	DEP	84-66-2	$C_{12}H_{14}O_4$	99.0
3	邻苯二甲酸二异丙酯	Diisopropylo-phthalate	DIPrP	605-45-8	$C_{14}H_{18}O_4$	98.5
4	邻苯二甲酸二烯丙酯	Diallyl phthalate	DAP	131-17-9	$C_{14}H_{14}O_4$	97.0
5	邻苯二甲酸二丙酯	Dipropyl phthalate	DPrP	131-16-8	$C_{14}H_{18}O_4$	98.0
6	邻苯二甲酸二异丁酯	Diisobutyl phthalate	DIBP	84-69-5	$C_{16}H_{22}O_4$	99.0
7	邻苯二甲酸二丁酯	Dibutyl phthalate	DBP	84-74-2	$C_{16}H_{22}O_4$	99.0
8	邻苯二甲酸二(2-甲氧基)乙酯	Bis(2-methoxyethyl)phthalate	DMEP	117-82-8	$C_{14}H_{18}O_6$	94.0
9	邻苯二甲酸二异戊酯	Di-iso-amyl phthalate	DIPP	605-50-5	$C_{18}H_{26}O_4$	99.5
10	邻苯二甲酸二(4-甲基-2-戊基)酯	Bis(4-methyl-2-pentyl)phthalate	BMPP	146-50-9	$C_{20}H_{30}O_4$	98.0
11	邻苯二甲酸二(2-乙氧基)乙酯	Bis(2-ethoxyethyl)phthalate	DEEP	605-54-9	$C_{16}H_{22}O_6$	99.5
12	邻苯二甲酸二戊酯	Dipentyl phthalate	DPP	131-18-0	$C_{18}H_{26}O_4$	99.2
13	邻苯二甲酸二己酯	Dihexyl phthalate	DHXP	84-75-3	$C_{20}H_{30}O_4$	99.0
14	邻苯二甲酸丁基苄基酯	Benzyl butyl phthalate	BBP	85-68-7	$C_{19}H_{20}O_4$	97.0
15	邻苯二甲酸二(2-丁氧基)乙酯	Bis(2-*n*-butoxyethyl)phthalate	DBEP	117-83-9	$C_{20}H_{30}O_6$	98.5
16	邻苯二甲酸二环己酯	Dicyclohexyl phthalate	DCHP	84-61-7	$C_{20}H_{26}O_4$	99.5
17	邻苯二甲酸二(2-乙基)己酯	Bis(2-ethylhexyl)phthalate	DEHP	117-81-7	$C_{24}H_{38}O_4$	99.0
18	邻苯二甲酸二庚酯	Di-*n*-heptyl phthalate	DHP	3648-21-3	$C_{22}H_{34}O_4$	97.0
19	邻苯二甲酸二苯酯	Diphenyl phthalate	DPhP	84-62-8	$C_{20}H_{14}O_4$	99.5
20	邻苯二甲酸二正辛酯	Di-*n*-octyl phthalate	DNOP	117-84-0	$C_{24}H_{38}O_4$	97.5
21	邻苯二甲酸二异壬酯	Diisononyl ortho-phthalate	DINP	68515-48-0	$C_{26}H_{42}O_4$	98.5
22	邻苯二甲酸二异癸酯	Diisodecyl ortho-phthalate	DIDP	26761-40-0	$C_{28}H_{46}O_4$	99.5
23	邻苯二甲酸二壬酯	Dinonyl phthalate	DNP	84-76-4	$C_{26}H_{42}O_4$	99.5

附 录 B
（资料性附录）
质谱参数

B.1 气相色谱-质谱参数

表 B.1 23 种邻苯二甲酸酯化合物 GC-MS 的特征离子

序号	化合物	保留时间/min	定性离子				丰度比
			1	2	3	4	
1	DMP	11.07	163*	77	135	194	100∶26∶9∶6
2	DEP	13.78	149*	121	177	222	100∶8∶21∶2
3	DIPrP	15.12	149*	167	209	105	100∶4∶4∶6
4	DAP	17.37	149*	76	132	189	100∶17∶28∶43
5	DPrP	17.99	149*	76	191	209	100∶5∶6∶6
6	DIBP	20.30	149*	167	205	223	100∶3∶2∶6
7	DBP	22.74	149*	121	205	223	100∶2∶3∶3
8	DMEP	23.75	59*	104	149	207	100∶8∶11∶5
9	DIPP	25.73	85*	69	149	167	100∶33∶96∶33
10	BMPP	25.81	149*	85	104	167	100∶23∶7∶9
11	DEEP	26.91	72*	149	104	176	100∶54∶29∶11
12	DPP	27.94	149*	104	219	237	100∶4∶2∶4
13	DHXP	32.30	149*	76	104	251	100∶2∶3∶8
14	BBP	32.56	149*	91	104	206	100∶74∶18∶20
15	DBEP	34.80	149*	85	101	193	100∶70∶82∶45
16	DCHP	35.91	149*	104	167	249	100∶4∶31∶6
17	DEHP	36.10	167*	104	149	279	19∶9∶100∶2
18	DHP	36.16	265*	104	247	149	5∶3∶2∶100
19	DPhP	36.57	225*	77	104	153	100∶22∶5∶4
20	DNOP	40.86	279*	149	167	261	3∶100∶3∶1
21	DINP	43.56	293*	127	149	167	8∶11∶100∶5
22	DIDP	45.73	307*	141	149	167	11∶14∶100∶5
23	DNP	45.95	293*	149	167	85	5∶100∶3∶4
* 定量离子。							

B.2 液相色谱-质谱/质谱参数[1)]

a) 气帘气压力(CUR):30 Psi(氮气);
b) 离子源喷雾电压(IS):5 500 V;
c) 雾化温度(TEM):550 ℃;
d) 雾化气压力(GAS1):50 Psi(氮气);
e) 加热辅助气(GAS2):50 Psi(氮气);
f) 碰撞气流速比(CAD):4;
g) 其他参数参见表 B.2。

表 B.2 23 种邻苯二甲酸酯化合物 LC-MS/MS 特征选择离子及质谱参数

序号	化合物	相对分子质量	参考保留时间	定性离子对	去簇电压/V	碰撞气能量/V
1	DMP	194.19	5.45	195.3/163.1*	105	14.3
				195.3/133.1	100	32
2	DMEP	282.30	5.52	283.4/207.1*	150	10
				283.4/59.1	150	16
3	DEEP	310.3	6.19	311.4/221.2*	150	10
				311.4/149	100	41
4	DEP	222.24	6.22	223.3/149.3*	130	24
				223.3/177.0	130	11.6
5	DAP	246.27	6.62	247.3/189.2*	150	11
				247.3/149.0	100	23
6	DIPrP	250.29	7.10	251.2/209.0*	70	13
				251.2/167.0	70	16
7	DPrP	250.29	7.29	251.2/149.0*	120	23
				251.2/191.1	120	13
8	DPhP	318.33	7.85	319.4/225.2*	100	14
				319.4/77.0	100	50
9	DIBP	278.35	8.99	279.4/223.2*	100	13
				279.4/267.2	100	15.5
10	BBP	312.36	9.06	313.3/205.1*	170	10.3
				313.3/149.1	170	18
11	DBEP	366.45	9.18	367.4/249.3*	130	11
				367.4/101.1	130	18
12	DBP	278.35	9.27	279.4/205.1*	140	11
				279.4/149.2	140	20

1) 非商业性声明:B.2 中所列参数是在 API 5000 质谱/质谱仪上完成的,此处列出的试验用仪器型号仅是为了提供参考,并不涉及商业目的,鼓励标准使用者尝试不同型号的仪器。

表 B.2（续）

序号	化合物	相对分子质量	参考保留时间	定性离子对	去簇电压/V	碰撞气能量/V
13	DIPP	306.4	11.74	307.4/219.2*	190	12
				307.4/237.2	100	13
14	DPP	306.4	11.97	307.4/167.2*	100	20
				307.4/149.1	190	16
15	DCHP	330.43	12.06	331.4/167.0*	170	20
				331.4/249.3	150	14
16	BMPP	334.43	12.87	335.5/167.2*	170	17
				335.5/251.4	170	12
17	DHXP	334.45	13.31	335.4/149.1*	210	21
				335.4/233.3	170	11
18	DHP	362.51	13.75	363.4/149.3*	170	21
				363.4/247.3	170	11
19	DEHP	390.56	14.04	391.3/148.7*	270	25
				391.3/113.0	250	14
20	DNOP	390.56	14.23	391.6/149.2*	190	19
				391.6/261.4	190	13
21	DINP	418.62	14.54	419.2/127.0*	150	17
				419.2/275.1	150	14
22	DNP	418.61	14.84	419.5/149.2	250	17
				419.5/275.4	200	14
23	DIDP	446.66	14.96	447.4/141.1*	190	15
				447.4/289.5	190	15
* 定量离子对。						

附 录 C
（资料性附录）
质 谱 图

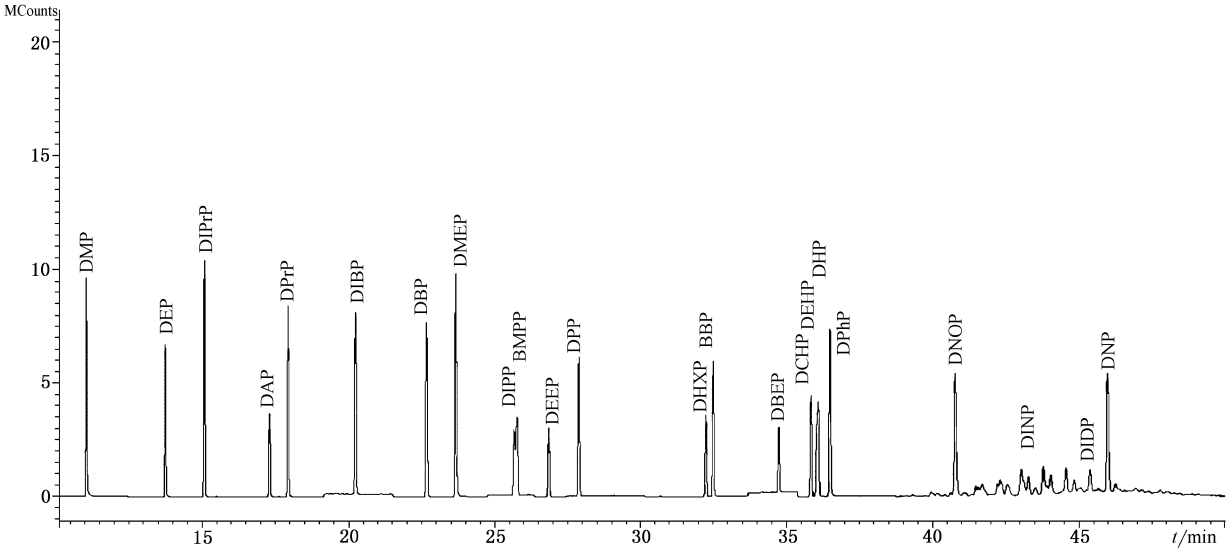


图 C.1 23 种邻苯二甲酸酯化合物标准品 GC-MS-SIM 图

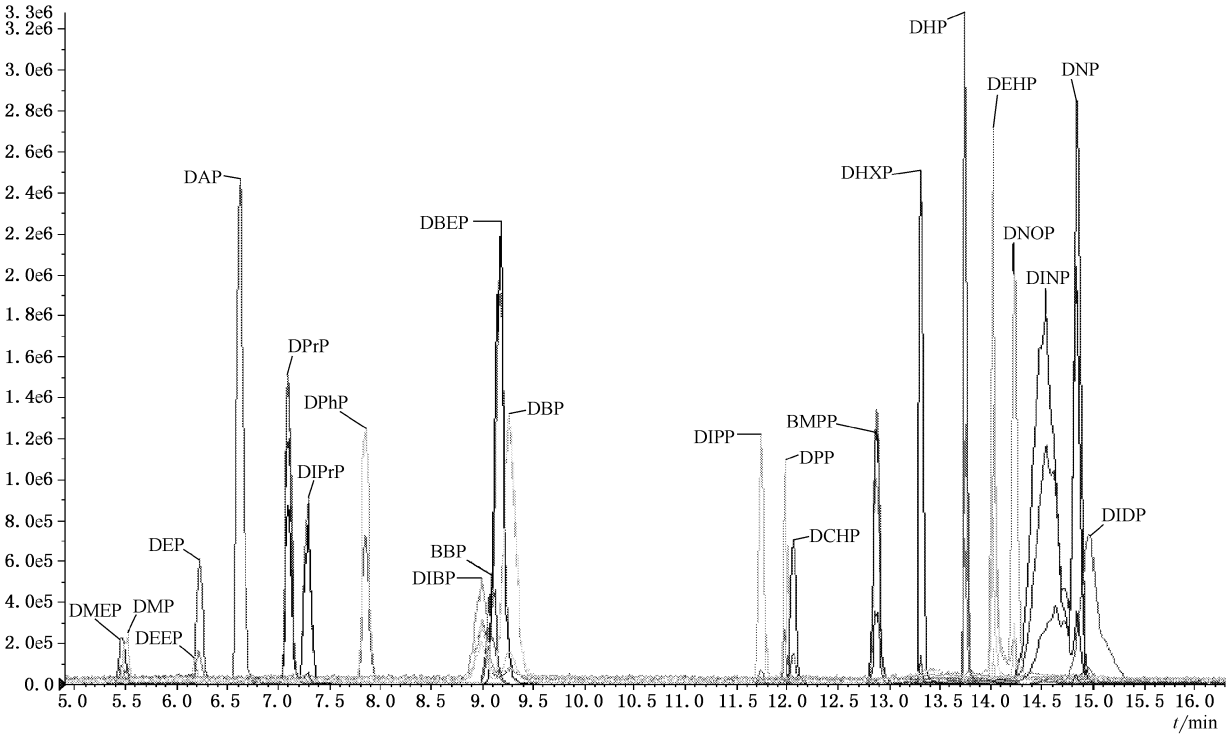


图 C.2 23 种邻苯二甲酸酯化合物标准品 LC-MS/MS 的总离子流图

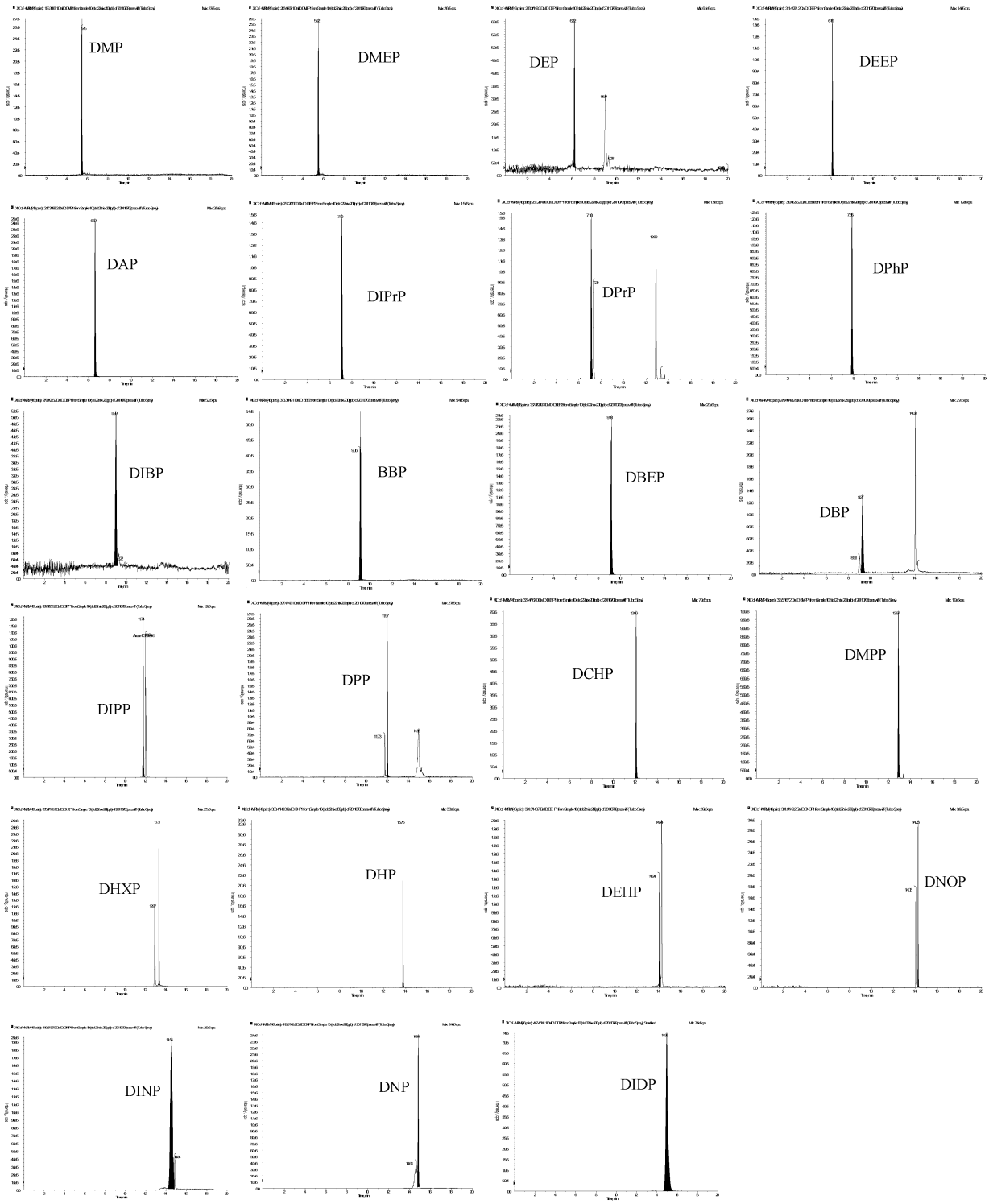


图 C.3　23 种邻苯二甲酸酯化合物标准品定量离子对的 MRM 图(LC-MS/MS)

附 录 D
（资料性附录）
23 种邻苯二甲酸酯的添加回收率数据

表 D.1 10 种食品中 23 种邻苯二甲酸酯的添加回收率数据(GC-MS 法)(n=6,平均回收率)

化合物	添加浓度 mg/kg	回收率/%									
		番石榴汁	固体乳酸菌饮料	调味精粉	葡萄果冻	柠檬香精	水果酥	柚子酱	鸡蛋面	食用橄榄油	木瓜牛奶
DMP	0.1	89.4	92.1	82.1	96.9	102.2	82.9	82.2	82.1	82.6	83.3
	1.0	98.6	83.3	93.3	96.2	101.4	90.3	95.3	96.8	99.3	95.3
	10.0	92.6	87.6	89.6	106.2	99.6	99.6	89.9	99.6	99.6	99.6
DEP	0.1	92.1	97.6	93.6	98.6	89.8	98.6	90.6	100.6	99.6	95.2
	1.0	97.7	97.4	85.4	99.6	104.2	95.5	88.4	86.4	86.4	86.4
	10.0	100.2	86.8	96.8	92.6	99.8	93.8	97.8	98.8	97.8	97.9
DIPrP	0.1	91.6	85.7	94.6	95.2	98.6	94.2	90.6	99.4	94.6	96.4
	1.0	98.8	93.6	92.2	95.4	95.7	98.2	99.2	90.2	94.2	92.2
	10.0	95.6	85.4	96.4	91.6	91.3	96.6	96.8	98.4	90.4	96.4
DAP	0.1	82.4	93.7	91.6	98.6	89.8	95.3	86.3	82.3	85.8	88.3
	1.0	97.6	102.3	98.8	95.6	88.2	92.3	92.4	82.1	92.4	92.2
	10.0	100.7	93.1	95.6	94.3	101.2	89.6	86.6	92.6	84.6	85.6
DPrP	0.1	89.5	97.5	99.5	101.4	90.6	89.5	89.4	89.4	89.9	89.2
	1.0	98.5	88.4	98.3	96.2	88.4	88.7	98.8	98.6	96.5	96.5
	10.0	93.6	104.7	99.6	96.5	97.8	96.2	96.6	92.6	91.6	94.6
DIBP	0.1	96.3	87.5	96.9	81.2	90.6	92.2	96.0	92.1	96.6	98.3
	1.0	94.7	97.9	96.2	95.6	99.2	98.7	98.7	97.7	97.7	94.5
	10.0	101.2	92.4	106.2	108.3	96.8	100.8	101.4	100.2	101.6	101.6
DBP	0.1	93.6	86.8	98.6	89.4	86.9	99.1	98.6	91.6	92.6	92.6
	1.0	98.7	97.7	99.6	98.8	101.2	102.6	95.7	98.8	98.8	97.7
	10.0	92.3	95.7	92.6	96.6	100.2	102.5	91.3	95.6	91.3	94.8
DIPP	0.1	93.6	102.0	98.9	96.0	102.4	92.6	89.8	82.4	95.8	89.8
	1.0	95.2	97.3	96.1	98.7	102.2	97.7	88.2	97.6	99.8	101.2
	10.0	89.4	83.3	96.6	101.4	95.8	94.8	101.2	100.7	100.4	101.1
DMEP	0.1	95.2	107.0	98.7	92.4	80.1	89.8	82.1	90.2	98.7	85.9
	1.0	103.1	113.1	95.8	89.8	96.8	101.2	85.6	102.3	95.8	104.4
	10.0	92.7	95.4	96.9	95.8	99.6	101.1	95.6	100.6	96.9	99.9

表 D.1（续）

化合物	添加浓度 mg/kg	回收率/%									
		番石榴汁	固体乳酸菌饮料	调味精粉	葡萄果冻	柠檬香精	水果酥	柚子酱	鸡蛋面	食用橄榄油	木瓜牛奶
BMPP	0.1	102.2	87.9	98.8	95.5	100.6	98.6	84.7	100.4	98.8	98.7
	1.0	101.4	93.5	96.8	92.3	86.4	95.6	85.8	101.5	96.8	105.5
	10.0	99.6	91.4	100.4	99.9	98.8	94.3	101.1	96.8	100.4	102.5
DEEP	0.1	89.8	94.2	95.8	92.2	95.2	81.2	88.9	85.6	95.8	89.7
	1.0	104.2	97.4	82.8	98.7	86.4	85.6	85.6	96.9	82.8	101.4
	10.0	99.8	94.9	99.6	100.8	97.9	86.2	102.5	100.1	99.6	101.1
DPP	0.1	92.4	94.1	102.2	99.1	96.4	90.1	92.4	82.2	102.2	92.9
	1.0	101.2	91.4	96.1	102.6	92.2	91.2	89.8	93.3	96.1	98.8
	10.0	96.8	107.4	100.1	102.5	96.4	102	95.8	96.8	100.1	93.3
DHXP	0.1	88.8	86.4	86.3	93.7	98.6	102.2	95.5	86.9	88.8	98.7
	1.0	102.2	97.7	98.5	102.3	95.7	94.5	92.3	101.2	90.9	91.1
	10.0	94.4	98.3	92.1	93.1	91.3	103.2	99.9	100.2	95.5	100.5
BBP	0.1	88.7	86.2	88.7	97.5	89.8	101.4	96.2	102.4	98.9	102.1
	1.0	94.8	97.2	94.8	88.4	88.2	96.2	102.2	102.2	102.8	101.1
	10.0	92.5	93.6	92.5	104.7	101.2	96.5	96.8	95.8	100.7	102.2
DBEP	0.1	98.7	93.4	88.8	98.8	98.9	81.2	102.4	84.5	82.8	98.7
	1.0	92.9	104.7	90.9	96.8	104.5	95.6	110.2	101.4	101.1	96.8
	10.0	100.3	101.2	95.5	100.4	99.7	108.3	81.2	102.8	101.6	102.8
DCHP	0.1	93.6	94.6	98.9	95.8	89.8	94.3	100.8	92.2	98.7	98.9
	1.0	102.5	102.5	102.8	82.8	106.1	80.9	97.6	98.7	98.9	108.2
	10.0	93.6	97.4	100.7	99.6	100.1	91.4	100.9	100.8	99.9	96.8
DHP	0.1	86.3	96.3	82.8	95.2	84.7	91.6	89.8	99.1	85.8	101.2
	1.0	89.7	99.7	101.1	86.4	85.8	88.6	101.4	102.6	101.4	96.6
	10.0	95.6	85.6	101.6	97.9	101.1	88.2	99.4	102.5	103.3	94.4
DEHP	0.1	86.9	92.3	98.7	96.4	88.9	87.7	94.1	98.7	96.8	88.9
	1.0	97.8	95.6	98.9	92.2	85.6	94.4	95.8	100.4	98.3	92.7
	10.0	101.2	86.5	99.9	96.4	102.5	96.6	102.2	101.2	100.5	96.8
DPhP	0.1	98.7	87.6	80.1	89.8	95.5	95.5	102.1	102.2	102.4	99.9
	1.0	103.2	93.4	96.8	104.2	98.2	98.2	85.5	101.4	98.7	91.9
	10.0	109.3	98.4	99.6	99.8	99.6	99.6	102.5	99.6	106.6	104.3
DNOP	0.1	98.2	83.5	100.6	92.4	92.4	92.4	103.4	89.8	92.4	95.8
	1.0	106.3	102.0	86.4	101.2	89.6	89.6	92.5	104.2	106.2	99.1
	10.0	98.7	98.7	98.8	96.8	109.6	101.6	104.5	99.8	99.6	100.4

表 D.1（续）

化合物	添加浓度 mg/kg	回收率/%									
		番石榴汁	固体乳酸菌饮料	调味精粉	葡萄果冻	柠檬香精	水果酥	柚子酱	鸡蛋面	食用橄榄油	木瓜牛奶
DINP	0.5	93.6	109.6	103.4	96.8	84.4	88.8	84.8	84.8	96.8	104.8
	1.0	94.7	83.2	99.4	84.5	86.9	82.6	98.7	92.4	95.2	98.9
	10.0	98.5	94.7	98.4	102.8	100.2	92.2	92.1	96.8	98.7	99.7
DIDP	0.5	86.6	93.6	89.8	97.4	82.8	104.4	100.8	101.4	91.2	85.4
	1.0	96.8	89.8	82.3	92.2	102.4	97.7	104.2	88.8	92.1	89.8
	10.0	103.6	87.4	92.6	100.8	95.8	92.5	100.1	94.4	95.8	100.1
DNP	0.1	79.6	89.6	78.6	102.3	105.6	98.6	89.3	78.6	80.2	90.3
	1.0	102.3	95.3	89.3	120.3	89.6	98.6	92.3	106.3	106.8	102.3
	10.0	89.6	89.2	103.6	112.6	98.3	85.3	89.6	103.6	98.6	104.3

表 D.2　10 种食品中邻苯二甲酸酯的添加回收率数据（LC-MS/MS 法）（n＝6，平均回收率）

化合物	添加浓度 mg/kg	回收率/%									
		番石榴汁	固体乳酸菌饮料	调味精粉	葡萄果冻	柠檬香精	水果酥	柚子酱	鸡蛋面	食用橄榄油	木瓜牛奶
DMP	0.1	98.1	92.8	92.8	89.5	96.6	84.1	94.6	89.6	92.1	97.6
	1	98.2	97.1	97.1	112	81.9	90.3	91.9	109	93.7	91.1
	10	97.7	92.15	92.15	103	102	99.6	93.4	96.4	99.6	93.4
DEP	0.1	97.4	84.2	84.2	83.5	98.7	94.3	88.7	89.7	93.6	89.7
	1	97.8	97.2	97.2	89.8	83.5	86.2	88.5	98.5	85.4	98.5
	10	97.89	97.81	97.81	91.1	95.4	99.8	97.4	97.2	98.8	97.2
DIPrP	0.1	99.3	79.5	79.5	78.8	85.7	99.6	95.7	95.7	99.6	95.7
	1	107.8	101.1	101.1	94.6	92.8	90.2	92.9	92.9	91.2	92.9
	10	100.1	101.1	101.1	95.1	101	100.4	100	100	86.4	100
DAP	0.01	93.2	97.3	97.3	97.8	81.3	86.5	91.3	91.3	96.5	91.3
	0.05	92.2	86.4	86.4	99.4	80.6	84.2	81	81	82.2	81
	1	99.8	89.8	89.8	98.1	98.1	94.3	93.1	93.1	94.6	93.1
DPrP	0.1	95.2	75.5	75.5	76.9	89.2	97.7	89.2	89.6	99.5	89.6
	1	96.8	86.8	86.8	101	79.8	92.5	99.8	109	99.1	109
	10	97.8	91.23	91.23	101	96.4	94.6	96.4	96.4	83.6	96.4
DIBP	0.1	97.2	93.8	93.8	83.7	98	96.3	98	98	96.3	98
	1	97.8	91.3	91.3	94.5	93.6	98.7	96.6	98.5	94.7	96.6
	10	94.89	94.11	94.11	92.1	95.1	104.2	94.2	97.2	101.2	94.2

表 D.2（续）

化合物	添加浓度 mg/kg	回收率/%									
		番石榴汁	固体乳酸菌饮料	调味精粉	葡萄果冻	柠檬香精	水果酥	柚子酱	鸡蛋面	食用橄榄油	木瓜牛奶
DBP	0.1	92.3	87.7	87.7	82.7	98.7	95.6	96.7	76.7	93.6	76.7
	1	94.8	91.8	91.8	94.8	94.5	98.6	94.1	84.1	94.7	84.1
	10	102.1	103.3	103.3	102.1	104	97.3	103	105	101.4	105
DIPP	0.1	93.3	83.5	83.5	93.6	115	97.7	114	91.4	91.9	114
	1	95.8	91.8	91.8	98.5	111	97.8	111	111	96.1	111
	10	100.2	101.2	101.2	92.2	94.3	108.4	94.3	94.3	86.6	94.3
DMEP	0.1	98.3	98.7	98.7	95	91.4	97.7	91.4	114	95.2	91.4
	1	93.8	112	112	105.4	112	96.8	112	110.5	96.4	112
	10	92.28	101.2	101.2	100.2	101.2	93.9	101.2	101.2	95.6	101.2
BMPP	0.1	93.8	95.4	95.4	96.7	95.4	98.9	95.4	95.4	91.6	95.4
	1	95.3	92.3	92.3	92.3	92.3	96.1	92.3	92.3	95.6	92.3
	10	92.28	92.38	92.38	92.3	92.4	102.4	92.4	92.4	84.3	92.4
DEEP	0.1	93.5	98.1	98.1	94.4	98.6	95.8	98.6	98.6	87.2	98.6
	1	91.3	91.2	91.2	81.2	91.2	82.8	91.2	91.2	95.6	91.2
	10	91.23	91.21	91.21	98.2	91.2	99.6	91.2	91.2	86.2	91.2
DPP	0.1	93.6	93.6	93.6	91.8	91.6	101.2	91.6	91.6	94.1	91.6
	1	94.6	84.5	84.5	83.1	83.1	96.7	83.1	83.1	91.2	83.1
	10	95.24	85.24	85.24	83.3	83.3	109.1	83.3	83.3	102	83.3
DHXP	0.1	99.1	91.9	91.9	83.6	88.5	89.8	88.7	88.7	102.2	88.7
	1	95.9	95.9	95.9	91.4	91.9	93.9	91.4	91.4	92.5	91.4
	10	98.71	91.71	91.71	91.5	91.7	96.5	91.7	91.7	101.2	91.7
BBP	0.1	94.9	94.9	94.9	93.5	84.6	98.9	84.6	79.6	94.5	84.6
	1	112.1	112.3	112.3	97.1	97.1	101.8	97.1	97.1	101.1	97.1
	10	98.99	98.91	98.91	99.5	98.1	98.7	98.1	98.1	103.8	98.1
DBEP	0.1	94.5	97.7	97.7	93.5	93.5	87.8	93.5	93.5	97.2	93.5
	1	112.1	111.1	111.1	112	112.1	101.1	112.1	112.1	97.7	112.1
	10	98.99	100.2	100.2	91	91	101.2	91	91	101.8	91
DCHP	0.1	93.7	98.3	98.3	92.8	92.5	98.7	92.5	92.5	93.1	92.5
	1	102.1	110.1	110.1	94.37	110	97.9	110	110	101.2	110
	10	98.21	98.21	98.21	97.3	97.21	91.9	97.21	97.21	107.5	97.21
DHP	0.1	98.8	89.6	89.6	87.2	79	88.8	79	79	98.1	79
	1	103.2	103.1	103.1	115	114.1	102.4	115.2	113.1	101.4	112.1
	10	98.24	91.24	91.24	96.5	99.91	93.3	99.91	99.91	100.2	99.91

表 D.2（续）

化合物	添加浓度 mg/kg	回收率/%									
		番石榴汁	固体乳酸菌饮料	调味精粉	葡萄果冻	柠檬香精	水果酥	柚子酱	鸡蛋面	食用橄榄油	木瓜牛奶
DEHP	0.1	93.9	92.8	92.8	81.6	81	97.8	81	81	101.3	81
	1	98.1	92.1	92.1	91.1	93.1	98.8	93.1	93.1	107.4	93.1
	10	98.5	97.5	97.5	91.8	92.91	102.5	92.91	92.91	99.9	92.91
DPhP	0.1	94.6	103	103	94.9	90.3	104.4	89.1	89.1	87.8	89.1
	1	99.3	94.1	94.1	112	102.3	91.7	102.3	102.3	103.2	102.3
	10	99.12	99.3	99.3	94.3	93.31	107.6	93.31	93.31	99.3	93.31
DNOP	0.1	92	91.7	91.7	91.4	94	96.3	94.4	94.6	99.4	94.6
	1	99.6	96.7	96.7	95.6	94.7	101.2	94.7	94.7	89.1	94.7
	10	99.79	102.1	102.1	105	103.1	96.6	103.1	103.1	101.6	103.1
DINP	0.1	103.4	83.6	83.6	83	106	102.8	90	90	90.8	95
	1	97.6	87.8	87.8	91.4	98	99.9	98	98	92.6	98
	10	99.89	91.9	91.9	86.1	100.1	98.7	100.1	100.1	97.2	100.1
DIDP	0.1	91.4	87.2	87.2	102	98	84.4	99.2	89.2	102.4	99.2
	1	109	99.6	99.6	95.6	93	99.8	93.5	95.5	98.7	93.5
	10	99.6	99.2	99.2	99.4	99.6	100.1	99.1	99.1	102.5	99.1
DNP	0.1	110.3	102.3	89.7	96.3	98.5	96.3	98.3	102.9	112.6	87.9
	1	98.6	101.2	98.6	89.6	103.6	88.9	78.9	86.9	86.3	84.9
	10	88.9	99.6	102.3	111.9	89.9	96.3	98.6	99.1	103.6	89.9

Foreword

This standard was drafted according to GB/T 1. 1—2009 Directives for standardization—Part 1: Structure and drafting of standards.

Please pay attention that some of the content of this document may involve patents, the publisher of this document does not assume the responsibility to identify these patents.

This standard was proposed by and is under the charge of the Certification and Accreditation Administration of the People's Republic of China.

This standard was drafted by Inspection & Quarantine Technology Center, Xiamen Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, Shenzhen Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, Fujian Inspection and Research Institute for Product Quality, and Jianxi Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China.

This standard was mainly drafted by Xu Dunming, Chen Luping, Fang Enhua, Huang Yonghui, Ye Gang, Lin Liyi, Huang Hongxia, Zheng Xianghua, Dai Ming, Sheng Jincan, Wei Yuanlong, Yang Lizhong, Zhang Jin, Guo Ping, Wu Min, Yue Zhenfeng, Zheng Xiaoyan, Zhou Yu.

Determination of phthalate esters(PAEs) in food for export

Method I GC-MS method

1 Scope

This standard specifies the determination and confirmation method of 23 phthalate esters by gas chromatography-mass spectrometry.

This standard is applicable to the determination and confirmation of dimethyl phthalate(DMP), diethyl phthalate(DEP), isopropyl phthalate (DIPrP), diallyl phthalate (DAP), phthalate Dipropyl (DPrP), isobutyl phthalate (DIBP), dibutyl phthalate (DBP), dibutyl phthalate (2-methoxy) ethyl (DMEP), phthalate dimethyl amyl(DIPP), phthalate(4-methyl-2-pentyl) ester(BMPP), phthalate(2-ethoxy) ethyl (DEEP), o amyl acetate phthalate(DPP), hexyl phthalate(DHXP), benzyl butyl phthalate esters(BBP), dibutyl phthalate (2-butoxy) ethyl (DBEP), dicyclohexyl phthalate esters (DCHP), phthalate (2-ethylhexyl) ester(DEHP), G phthalate esters(DHP), diphenyl phthalate(diphenyl, DPhP), *n*-octyl phthalate(DNOP), isononyl phthalate ester(DINP), isodecyl phthalate ester(DIDP), dinonyl phthalate (DNP)(Table A. 1) in liquid beverages, solid drink, jam, pulp, jelly, spices, flavors and fragrances, fats and oils, dairy products, flour and starch-based products, and pastries.

2 Principle

After extraction and purification, the analytes in various types of food are determined by gas chromatography-mass spectrometry with selected ion monitoring scan mode(SIM), qualitatived by the retention time(RT) and ion abundance, and quantitatived by external standard method with the peak area of quantitative ion in standard sample.

3 Reagents and materials

Unless specified, all the reagents used shall be analytically pure(stored in the glass bottom to avoid contacting plastics), and "water" used here is distilled water.

3.1 *n*-hexane: HPLC grade.

3.2 Acetonitrile: HPLC grade.

3.3 Methanol: HPLC grade.

3.4 Acetone: HPLC grade.

3.5 Sodium chloride.

3.6 Magnesium sulfate: HPLC grade.

3.7 Sodium acetate: HPLC grade.

3.8 PSA powder: grain size 40 or 120 μm, pore diameter 60 Å.

3.9 C_{18} powder: grain size 40 or 120 μm, pore diameter 60 Å.

3.10 SPE cartridge: ProElut PSA glass column(1 g, 6 mL), conditioned using 5 mL acetone and 5 mL *n*-hexane before usage.

3.11 Standard substance: see Table A.1 in Annex A.

3.12 Standard stock solution: Accurately weigh an adequate amount of standards above(accurate to 0.1mg), to dissolve with *n*-hexane to form a standard stock solution of 1 000 mg/L in concentration, and then store in dark place at 4 ℃.

3.13 Standard working solution: Dilute the standard stock solution with *n*-hexane to the intended concentration of 0.1, 0.5, 1.0, 2.0, 5.0, 10.0 mg/L, respectively. These solutions shall be prepared before use.

4 Apparatus and equipment

4.1 GC-MS: equipped with electro-impact source(EI).

4.2 Electronic balance: accurate to 0.1 mg and 0.01 g.

4.3 Centrifuge: >4 000 r/min.

4.4 Nitrogen Evaporators.

4.5 Oscillator.

4.6 Whirlpool mixer.

4.7 Homogenizer: 18 000 r/min.

4.8 Ultrasonic extractor.

4.9 Tissue blender.

4.10 freezer Centrifuge:＞4 000 r/min.

5 Sample preparation and storage

5.1 Preparation of test samples

5.1.1 Solid,semisolid,and liquid samples

At least take 3 wholly packed samples from the same set(the gross quantity of the solid sample is 100 g －500 g after mixing and 100 mL －500 mL for liquid sample),put into glass container,and crush up the solid and semisolid sample to conformity and mix the liquid sample thoroughly as to be weighed.

5.1.2 Capsule,tablet form and powder samples

Take approximately 500 g of representative sample, to crush with a crusher and to grind into powder,and mix thoroughly. Put in clean glass containers,to seal and label them.

5.2 Storage of test samples

The test samples in powder form stored be stored at 0-4 ℃,and other test samples shall be frozen and stored below －18 ℃.

Precaution measures shall be taken to avoid contamination or other factors may cause the change of residues concentration in samples while sampling and preparing samples.

6 Method of determination

6.1 Pretreatment

6.1.1 Liquid samples

6.1.1.1 Hard-emulsified liquid sample

Accurately weigh an adequate amount of 5.0 g(accurate to 0.01 g)of the mixed liquid sample(carbon dioxide shall be eliminated if contained)into a 25 mL glass tube,add sodium chloride until the water layer saturated,and add 5 mL *n*-hexane,vortex for 1 min,centrifuge for 2 min at speed of 4 000 r/

min. and take the upper *n*-hexane layer for GC-MS analysis.

6.1.1.2 Liquid sample easy to emulsify

Accurately weigh an adequate amount of 5.0 g(accurate to 0.01 g)of the mixed liquid sample(carbon dioxide shall be eliminated if contained)into a 25 mL glass tube,add 10 mL acetonitrile. Vortex for 1 min. Centrifuge for 2 min at speed 4 000 rpm. Take the upper layer into a 25 mL glass centrifuge tube,add sodium chloride until the water layer saturated,and vortex for 1 min,to settle down or centrifuge to make it stratify. Take the upper acetonitrile layer into another glass tube,nitrogen evaporate it to nearly dry,and constant volume to 5 mL with *n*-hexane for GC-MS analysis.

6.1.2 Non-oily solid and semisolid samples

Accurately weigh an adequate amount of 5.0 g(accurate to 0.01g)of the mixed test sample into a glass tube with 50 mL ground glass stopper,add 10 mL water(increase the amount of water depending on sample moisture content). Add sodium chloride until the water layer saturated. Add 10 mL acetonitrile,to vortex for 1 min,ultrasonically extract for 20 min,centrifuge for 2 min at speed of 4 000 r/min,collect supernatant fluid. Repeated once,and combined all supernatant,to evaporatedto nearly dry at 40℃ with nitrogen,and constant volume to 5 mL with *n*-hexane for GC-MS analysis.

6.1.3 Oily samples

Accurately weigh a mixed test sample 1.0 g(accurate to 0.01 g)into a 25 mL glass tube with ground glass stopper . Add 5 mL acetonitrile,vortex for 1 min,centrifuge for 2 min at speed 4 000 r/min,and collect supernatant fluid. Repeated once,and combined all supernatant,to evaporatedto nearly dry at 40 ℃ with nitrogen,and constant volume to 1 mL with methanol. Freeze for 2 h at 4℃ in the refrigerator,centrifuge for 2 min at speed 4 000 r/min. Take the upper layer into another glass tube for GC-MS.

6.1.4 QuEChERS method

The following method is optional for the samples in Section 6.1.2 and 6.1.3:Accurately weigh an adequate amount of 5.0 g(accurate to 0.01g)of the mixed test sample into a glass tube with 50 mL ground glass stopper,add 5 mL water(there is no need to add water for aqueous sample),add 15 mL acetonitrile exactly. Add 6 g $MgSO_4$ and 1.5 g sodium acetate. Vortex for 1 min. Centrifuge for 2 min at speed 4 000 r/min. Take the upper layer. Evaporate it at 40℃ to nearly dry. Constant volume to 5 mL with acetonitrile. Add 50 mg PSA powder(3.8),50 mg C_{18} powder(3.9),150 mg $MgSO_4$,to vortex for 1 min. Centrifuge for 2 min at speed 4 000 r/min. Take the upper layer for GC-MS analysis.

6.1.5 SPE method

The following method is optional for the samples in Section 6.1.2 and 6.1.3:Weigh 1.0 g samples in glass tubes,add 2 mL *n*-hexane and 10 mL acetonitrile,vortex for 2 min to mix thoroughly,then cen-

trifuge the sample under 4 000 r/min for 2 min, collect the lower phase. Add 10 mL acetonitrile to sample, then repeat the extraction process, combine the twice lower phases and concentrated to dry under nitrogen at 40℃. Add 2 mL *n*-hexane to dissolve the residue (extract) for SPE cleanup. And then, add the extract in SPE cartridge, control the flow at about 1 mL/min and collect the eluate; And then, 5 mL *n*-hexane and 5 mL 4% acetone in *n*-hexane were used for elution, and collect the eluate; to combine the eluates and concentrate to approach dryness under nitrogen at 40℃, dissolve the residue with 1 mL *n*-hexane for GC-MS.

6.2 Determination

6.2.1 GC-MS condition

GC-MS condition is as following:

a) Chromatographic column: TG/DB-5MS capillary column, 60 m × 0.25 mm i.d., 0.25 μm (film thickness) or equivalent;

b) Injection port temperature: 280 ℃;

c) Carrier gas: Helium, purity ≥ 99.999%, constant current mode, flow rate: 1.5 mL/min;

d) Ion source temperature: 250℃;

e) Electron ionization mode: EI, 70 eV;

f) Transfer temperature: 300℃;

g) Electron impact ionization source (EI), selected ion monitoring (SIM) (Table B.1 in Annex B and table 1);

h) Solvent delay time: 10 min;

i) Injection volume: 1.0 μL;

j) Injection mode: Splitless.

Table 1—Select ion group

No.	Time/min	Select Ion(m/z)
1	10.5	77,135,163,194
2	12.4	149,177,121,222
3	14.5	149,167,209

Table 1 (continued)

No.	Time/min	Select Ion(m/z)
4	16.2	104,132,149,189
5	17.7	76,149, 191,209
6	19.1	149,167,205,223
7	21.5	121,149,223,205
8	23.2	59,104,149, 207
9	24.7	69,85,104,149,167,251
10	26.4	72,149,176,193
11	27.4	104,149,219,237
12	30.1	76,91,149,104,206,251
13	33.7	85,101,149,193
14	35.4	104,149,167,247,249,265,279
15	36.4	77,104,153,225
16	38.7	149,167,261,279
17	40.9	127,141,149,167,261,279,293,307

6.2.2 Chromatographic separation conditions

Temperature program which can better separate target analytes is shown in Table 2.

Table 2—GC temperature program

	Rate ℃/min	Temperature ℃	Hold time min
Initial	—	60	1.00
Stage 1	30.0	160	1.00
Stage 2	3.5	220	2.00
Stage 3	5.0	270	5.00
Stage 4	2.0	280	7.00
Stage 5	10.0	300	1.00

6.2.3 GC-MS detection

According to the approximate concentration of the phthalic acid ester in the sample solution, select the similar standard working solution. The standard working solution shall be randomly injected in-between the injections of the sample solution at equal volume. The responses of every analytes in the standard working solution and sample solution shall be within the linear range of the instrumental detection. Under the above GC-MS condition, the retention time of phthalic acid esters is listed in Table

B. 1 in Annex B. and the GC-MS chromatogram(TIC)of phthalic acid esters, see figure C. 1 in Annex C. If the deviation of retention time of the analyte between test sample and standard solution is within ±0. 5% under the same experiment conditions, and the difference of relative ion ratio of the analyte between test sample and standard solution is also within the error allowed(the maximum deviation allowed for relative ion ratio are listed in table 3), corresponding the analyte would be considered to be in the sample.

Table 3—Maximum permitted tolerances for relative ion intensities using a range of mass spectrometric techniques

Relative intensity (% of base peak)	>50%	>20% to 50%	>10% to 20%	≤10%
Maximum permitted tolerances	±10%	±15%	±20%	±50%

6.3 Blank test

According to 6. 1-6. 3 to perform the blank testing without samples.

7 Quality Control

7.1 Sampling and preparation

Sampling tools shall be made stainless steel or glass, to avoid contacting with plastics.

7.2 Organic solvents

All organic solvents used in this standard, shall be carried out blank experiment before use. If the background is higher than the limit of quantification, the organic solvent shall be distilled until the background is lower than the limit of quantification.

7.3 Glasswares

Flush all of the glassware to be used with distilled water for 3 times after cleaning up, then steep into acetone for 1 hour, dry at 200℃ for 2 hours, and cool to room temperature for usage.

8 Calculation and expression of the result

Calculate the content of per phthalic acid ester in the test sample by GC-MS data processor or according to the formula. Background value shall be deducted.

$$X_i = \frac{A_i \times c_i \times V}{A_{is} \times m} \quad \cdots\cdots (1)$$

Where:

X_i ——the content of per phthalic acid ester in the test sample, mg/kg;

A_i ——the peak area(height)of per phthalic acid ester in the sample solution;

c_i ——the concentration of per phthalic acid ester in the standard working solution, μg/mL;

V ——the final volume of the sample solution, mL;

A_{is}——the peak area(height)of per phthalic acid ester in the standard working solution;

m ——the corresponding mass of the test sample in the final sample solution, g.

9 Limit of quantification and recovery

9.1 Limit of quantification(LOQ)

The method limits of quantification(LOQ)are 0.5 mg/kg for DINP and DIDP, and 0.1 mg/kg for other analytes.

9.2 Recovery

With different spiked concentrations in various matrixes, including guava juice, solid lactic acid bacteria beverage, adjustable gourmet powder, grape jelly, lemon essence, fruit cake, grapefruit sauce, egg surface, edible olive oil, papaws milk, the recovery data for phthalic acid ester in foodstuffs are listed in Table D.1 of Annex D.

Method Ⅱ LC-MS/MS method

10 Scope

This standard specifies the methods of sample preparation and qualified determination by high performance liquid chromatography-tandem mass spectrometry of 23 phthalic acid esters in food for export.

This standard is applicable to the determination and confirmation of dimethyl phthalate(DMP), diethyl

phthalate(DEP), isopropyl phthalate (DIPrP), diallyl phthalate (DAP), phthalate Dipropyl (DPrP), isobutyl phthalate (DIBP), dibutyl phthalate (DBP), dibutyl phthalate (2-methoxy) ethyl (DMEP), phthalate dimethyl amyl(DIPP), phthalate(4-methyl-2-pentyl) ester(BMPP), phthalate(2-ethoxy) ethyl (DEEP), o amyl acetate phthalate(DPP), hexyl phthalate(DHXP), benzyl butyl phthalate esters(BBP), dibutyl phthalate (2-butoxy) ethyl (DBEP), dicyclohexyl phthalate esters (DCHP), phthalate (2-ethylhexyl) ester (DEHP), G phthalate esters (DHP), diphenyl phthalate (diphenyl, DPhP), *n*-octyl phthalate(DNOP), isononyl phthalate ester(DINP), isodecyl phthalate ester(DIDP), dinonyl phthalate (DNP) (Table A. 1) in liquid beverages, solid drink, jam, pulp, jelly, spices, flavors and fragrances, fats and oils, dairy products, flour and starch-based products, and pastries.

11 Principle

Phthalic acid esters in the test samples are extracted with acetonitrile, and the residues are determined by liquid chromatography-mass spectrometry, quantified by external standard method.

12 Reagents and materials

Unless specified, all the reagents used shall be analytically pure (stored in the glass bottom to avoid contacting plastics), and "water" is distilled water.

12.1 Methanol: HPLC grade.

12.2 Acetonitrile: HPLC grade.

12.3 *n*-hexane: HPLC grade.

12.4 Acetone: HPLC grade.

12.5 NaCl.

12.6 Magnesium sulfate: HPLC grade.

12.7 Sodium acetate: HPLC grade.

12.8 PSA powder: As Part 3.8.

12.9 C_{18} powder: As Part 3.9.

12.10 SPE cartridge: As Part 3.10.

12.11 Formic acid.

12.12 0.1% Methanol in water(V/V): Mix 1 mL methanol and 999 mL water.

12.13 Standard substance: As Part 3.11.

12.14 Standard stock solution: Accurately weigh an adequate amount of standards above (accurate to 0.1 mg), to dissolve with methanol to form a standard stock solution of 100 mg/L in concentration.

12.15 Standard working solution: Dilute the standard stock solution with methanol to the intended concentration of 0.01mg/L to 1.0 mg/L, respectively.

13 Apparatus and equipment

13.1 Liquid chromatography-mass spectrometry, equipped with EIS ion source.

13.2 Electronic balance: accurate to 0.1 mg. and 0.01 g.

13.3 Centrifuge: >4 000 r/min.

13.4 Homogenizer: 18 000 r/min.

13.5 Ultrasonic extraction apparatus.

13.6 Oscillator.

13.7 Nitrogen Evaporators.

13.8 Turbine mixer.

13.9 Tissue blender.

13.10 freezer Centrifuge: >4 000 r/min.

14 Sample preparation and storage

14.1 Sample preparation

Same as Section 5.1.

14.2 Sample storage

Same as Section 5.2.

15 Method of determination

15.1 Pretreatment

15.1.1 Liquid samples

15.1.1.1 Hard-emulsified liquid sample

Accurately weigh an adequate amount of 5.0 g(accurate to 0.01 g)of the mixed liquid sample(carbon dioxide shall be eliminated if contained)into a glass tube of 25 mL,add sodium chloride until the water layer saturated,add 5.0 mL acetonitrile. To vortex for 1 min,centrifuge for 2 min at the speed 4 000 r/min,and take acetonitrile layer for LC-MS/MS analysis.

15.1.1.2 Easy-emulsified liquid sample

Accurately weigh an adequate amount of 5.0 g(accurate to 0.01g)of the mixed liquid sample(carbon dioxide shall be eliminated if contained)into a 25 mL glass tube,add 10 mL acetonitrile. Vortex for 1 min,centrifuge for 2 min at hightest speed 4 000 r/min. To take the upper layer into a glass centrifuge tube; add sodium chloride until saturating the water layer,vortex for 1 min,standing or centrifuge to make it stratify. Take the upper acetonitrile layer into another glass tube,evaporate it to nearly dry under nitrogen flow. Constant volume to 5 mL with acetonitrile for LC-MS/MS analysis.

15.1.2 Non-oily solid or semi-solid samples

Same as Section 6.1.2,but only evaporate to nearly dry,Constant volume to 5 mL with acetonitrile for LC-MS/MS analysis.

15.1.3 Oily samples

Same as Section 6.1.3,the analytes performed by LC - MS/MS.

15.1.4 QuEChERS method

The following method is optional for the samples in Section 15.1.2 and Section 15.1.3:Same as the Section 6.1.4,the analytes performed by LC-MS/MS.

15.1.5 SPE method

The following method is optional for the samples in Section 15.1.2 and Section 15.1.3:Same as the Section 6.1.5,but only evaporate to nearly dry,Constant volume to 5 mL with acetonitrile for LC-MS/MS analysis.

15.2 Determination

15.2.1 HPLC operating conditions

HPLC operating conditions is as following:

a) Column Ⅰ: Poroshell 120 EC-C_{18} column, 100 mm × 4.6 mm, 2.7 μm (diameter); Column Ⅱ: Accucore RP-MS cplumn, 100 mm × 2.1 mm, 2.6 μm (diameter); or equivalent.

b) Mobile phase: methanol-0.1% formic acid, the elution gradient is listed in Table 4;

c) Flow rate: see Table 4;

d) Column temperature: 35 ℃;

e) Injection volume: 10 μL.

Table 4—Elution gradient for HPLC

Time (min)	A 0.1% formic acid (%)	B Methanol (%)	Flow rate (mL/min)
Poroshell 120 EC-C_{18} column, 100 mm × 4.6 mm, 2.7 μm (diameter)			
0	30	70	0.7
4.0	5	95	0.7
6.0	5	95	0.7
6.1	0	100	0.7
11.0	0	100	0.7
11.1	30	70	0.7
15.0	30	70	0.7
Accucore RP-MS column, 100 mm × 2.1 mm, 2.6 μm (diameter)			
0	60	40	0.3
12.0	0	100	0.3
15.0	0	100	0.3
15.1	60	40	0.3
18.0	60	40	0.3

15.2.2 MS operating conditions

MS operating conditions is as following:

a) Ionization mode: ESI positive ion mode (ESI^+);

b) MS scan mode:multiple reaction monitoring(MRM);

c) Resolution:unit mass resolution;

d) Other MS conditions:see Section B.2 in Annex B.

15.2.3 LC/MS/MS determination

Under the optimized instrument working condition,according to the approximate concentration of analytes in the test sample solution,the standard working solution is selected with similar response to that of sample solution. The standard working solution shall be injected randomly in between the injections of sample solution of equal volume. Different matrix calibration solutions are injected into the instrument in a separate run. Using peak area as y-axis and concentration as x-axis,the content of phthalic acid esters in sample is quantified by standard calibration curve. The response of phthalic acid esters in the standard working solution and sample solution shall be in the linear range of the instrumental detection. Under the above LC-MS/MS condition,the retention time of phthalic acid esters is listed in Table B.2 in Annex B. The multiple reaction monitoring(MRM)chromatograms of standard working solution are showed in Figure C.2 and C.3 of Annex C.

If the deviation of retention time of the analyte between test sample and standard solution is the same under the same experiment conditions,and the difference of relative ion ratio of the analyte between test sample and standard solution is also within the error allowed(the maximum deviation allowed for relative ion ratio are listed in Table 5),corresponding the analyte would be considered to be in the sample.

Table 5—Maximum deviation allowed for relative ion ratio in qualitative determination

Relative ion ratio	>50%	>20% to 50%	>10% to 20%	≤10%
Max deviation allowed	±20%	±25%	±30%	±50%

15.3 Blank test

According to 15.1-15.3 to perform the blank testing without samples.

16 Quality Control

Same as Part 7.

17 Calculation and expression of result

Use chromatographic data processor or press(2)to calculate the concentration of test in the sample:

$$X = \frac{A \times c_s \times V}{A_s \times m} \quad \cdots\cdots(2)$$

Where:

X ——the content of each test substance in the sample, mg/kg;

A ——the peak area of each test substance in the sample;

c_s ——the concentration of each test substance in the standard working solution, μg/mL;

V ——the final volume of sample solution, mL;

A_s——the peak area of each test substance in the standard working solution;

m ——sample volume which the final sample solution represents, g.

notice: Background value shall be deducted.

18 Limit of quantification and recovery

18.1 Limit of quantification(LOQ)

The method limits of quantification(LOQ) are 0.01 mg/kg for DAP, and 0.1 mg/kg for other analytes.

18.2 Recovery

With different spiked concentrations in various matrixes, including guava juice, solid lactic acid bacteria beverage, adjustable gourmet powder, grape jelly, lemon essence, fruit cake, grapefruit sauce, egg surface, edible olive oil, papaws milk, the recovery data for phthalic acid ester in foodstuffs are listed in Table D.2 of Annex D.

Annex A
(normative)
The information of 23 phthalate esters(PAEs)

Table A. 1—The chemical information of 23 phthalate esters

No	Compound	Abbr.	CAS No.	Molecular formula	Purity ≥(%)
1	Dimethyl phthalate	DMP	131-11-3	$C_{10}H_{10}O_4$	99.5
2	Diethyl phthalate	DEP	84-66-2	$C_{12}H_{14}O_4$	99.0
3	Diisopropylo-phthalate	DIPrP	605-45-8	$C_{14}H_{18}O_4$	98.5
4	Diallyl phthalate	DAP	131-17-9	$C_{14}H_{14}O_4$	97.0
5	Dipropyl phthalate	DPrP	131-16-8	$C_{14}H_{18}O_4$	98.0
6	Diisobutyl phthalate	DIBP	84-69-5	$C_{16}H_{22}O_4$	99.0
7	Dibutyl phthalate	DBP	84-74-2	$C_{16}H_{22}O_4$	99.0
8	Bis(2-methoxyethyl)phthalate	DMEP	117-82-8	$C_{14}H_{18}O_6$	94.0
9	Di-iso-amyl phthalate	DIPP	605-50-5	$C_{18}H_{26}O_4$	99.5
10	Bis(4-methyl-2-pentyl)phthalate	BMPP	146-50-9	$C_{20}H_{30}O_4$	98.0
11	Bis(2-ethoxyethyl)phthalate	DEEP	605-54-9	$C_{16}H_{22}O_6$	99.5
12	Dipentyl phthalate	DPP	131-18-0	$C_{18}H_{26}O_4$	99.2
13	Dihexyl phthalate	DHXP	84-75-3	$C_{20}H_{30}O_4$	99.0
14	Benzyl butyl phthalate	BBP	85-68-7	$C_{19}H_{20}O_4$	97.0
15	Bis(2-*n*-butoxyethyl)phthalate	DBEP	117-83-9	$C_{20}H_{30}O_6$	98.5
16	Dicyclohexyl phthalate	DCHP	84-61-7	$C_{20}H_{26}O_4$	99.5
17	Bis(2-ethylhexyl)phthalate	DEHP	117-81-7	$C_{24}H_{38}O_4$	99.0
18	Di-*n*-heptyl phthalate	DHP	3648-21-3	$C_{22}H_{34}O_4$	97.0
19	Diphenyl phthalate	DPhP	84-62-8	$C_{20}H_{14}O_4$	99.5
20	Di-*n*-octyl phthalate	DNOP	117-84-0	$C_{24}H_{38}O_4$	97.5
21	Diisononyl ortho-phthalate	DINP	68515-48-0	$C_{26}H_{42}O_4$	98.5
22	Diisodecyl ortho-phthalate	DIDP	26761-40-0	$C_{28}H_{46}O_4$	99.5
23	Dinonyl phthalate	DNP	84-76-4	$C_{26}H_{42}O_4$	99.5

Annex B
(informative)
Mass spectrometry conditions

B.1 GC-MS conditions

Table B.1—The retention time, determination and confirmation selected monitoring ion of 23 phthalate esters

No.	Compound	Tr/min	Characteristic fragment ion(*amu*)				Abundance ration
			1	2	3	4	
1	DMP	11.07	163*	77	135	194	100∶26∶9∶6
2	DEP	13.78	149*	121	177	222	100∶8∶21∶2
3	DIPrP	15.12	149*	167	209	105	100∶4∶4∶6
4	DAP	17.37	149*	76	132	189	100∶17∶28∶43
5	DPrP	17.99	149*	76	191	209	100∶5∶6∶6
6	DIBP	20.30	149*	167	205	223	100∶3∶2∶6
7	DBP	22.74	149*	121	205	223	100∶2∶3∶3
8	DMEP	23.75	59*	104	149	207	100∶8∶11∶5
9	DIPP	25.73	85*	69	149	167	100∶33∶96∶33
10	BMPP	25.81	149*	85	104	167	100∶23∶7∶9
11	DEEP	26.91	72*	149	104	176	100∶54∶29∶11
12	DPP	27.94	149*	104	219	237	100∶4∶2∶4
13	DHXP	32.30	149*	76	104	251	100∶2∶3∶8
14	BBP	32.56	149*	91	104	206	100∶74∶18∶20
15	DBEP	34.80	149*	85	101	193	100∶70∶82∶45
16	DCHP	35.91	149*	104	167	249	100∶4∶31∶6
17	DEHP	36.10	167*	104	149	279	19∶9∶100∶2
18	DHP	36.16	265*	104	247	149	5∶3∶2∶100
19	DPhP	36.57	225*	77	104	153	100∶22∶5∶4
20	DNOP	40.86	279*	149	167	261	3∶100∶3∶1
21	DINP	43.56	293*	127	149	167	8∶11∶100∶5
22	DIDP	45.73	307*	141	149	167	11∶14∶100∶5
23	DNP	45.95	293*	149	167	85	5∶100∶3∶4
Those ions with"*"for quantitation.							

B.2 LC-MS/MS parameters

a) air curtain gas pressure(CUR):30 Psi(nitrogen);

b) ion source spray voltage(IS):5 500 V;

c) atomization temperature(TEM):550 ℃;

d) atomization gas pressure(GAS1):50 Psi(nitrogen);

e) heated auxiliary gas(GAS2):50 Psi(nitrogen);

f) collision flow ratio(CAD):4;

g) other parameters in Table B. 2

Table B. 2—Mass spectrometry characteristics parameters of 23 kinds of phthalate esters by LC-MS/MS

Number	compound	molecular weight	retention time	Characterization of ion-pair	To cluster voltage/V	Collision gas energy/V
1	DMP	194. 19	5. 45	195. 3/163. 1*	105	14. 3
				195. 3/133. 1	100	32
2	DMEP	282. 30	5. 52	283. 4/207. 1*	150	10
				283. 4/59. 1	150	16
3	DEEP	310. 3	6. 19	311. 4/221. 2*	150	10
				311. 4/149	100	41
4	DEP	222. 24	6. 22	223. 3/149. 3*	130	24
				223. 3/177. 0	130	11. 6
5	DAP	246. 27	6. 62	247. 3/189. 2*	150	11
				247. 3/149. 0	100	23
6	DIPrP	250. 29	7. 10	251. 2/209. 0*	70	13
				251. 2/167. 0	70	16
7	DPrP	250. 29	7. 29	251. 2/149. 0*	120	23
				251. 2/191. 1	120	13
8	DPhP	318. 33	7. 85	319. 4/225. 2*	100	14
				319. 4/77. 0	100	50
9	DIBP	278. 35	8. 99	279. 4/223. 2*	100	13
				279. 4/267. 2	100	15. 5
10	BBP	312. 36	9. 06	313. 3/205. 1*	170	10. 3
				313. 3/149. 1	170	18
11	DBEP	366. 45	9. 18	367. 4/249. 3*	130	11
				367. 4/101. 1	130	18
12	DBP	278. 35	9. 27	279. 4/205. 1*	140	11
				279. 4/149. 2	140	20

Non-commercial statement: the reference mass parameters in Section B. 2 are accomplished by API 5 000 LC/MS/MS. The equipment and its type involved in the standard method is only for reference and not related to any commercial aim, and the analysts are encouraged to use equipments of different corporation or different types.

Table B. 2（continued）

Number	compound	molecular weight	retention time	Characterization of ion-pair	To cluster voltage/V	Collision gas energy/V
13	DIPP	306. 4	11. 74	307. 4/219. 2*	190	12
				307. 4/237. 2	100	13
14	DPP	306. 4	11. 97	307. 4/167. 2*	100	20
				307. 4/149. 1	190	16
15	DCHP	330. 43	12. 06	331. 4/167. 0*	170	20
				331. 4/249. 3	150	14
16	BMPP	334. 43	12. 87	335. 5/167. 2*	170	17
				335. 5/251. 4	170	12
17	DHXP	334. 45	13. 31	335. 4/149. 1*	210	21
				335. 4/233. 3	170	11
18	DHP	362. 51	13. 75	363. 4/149. 3*	170	21
				363. 4/247. 3	170	11
19	DEHP	390. 56	14. 04	391. 3/148. 7*	270	25
				391. 3/113. 0	250	14
20	DNOP	390. 56	14. 23	391. 6/149. 2*	190	19
				391. 6/261. 4	190	13
21	DINP	418. 62	14. 54	419. 2/127. 0*	150	17
				419. 2/275. 1	150	14
22	DNP	418. 61	14. 84	419. 5/149. 2	250	17
				419. 5/275. 4	200	14
23	DIDP	446. 66	14. 96	447. 4/141. 1*	190	15
				447. 4/289. 5	190	15
* The ion pair for quantitaion.						

Annex C
(informative)
MS Chromatograms

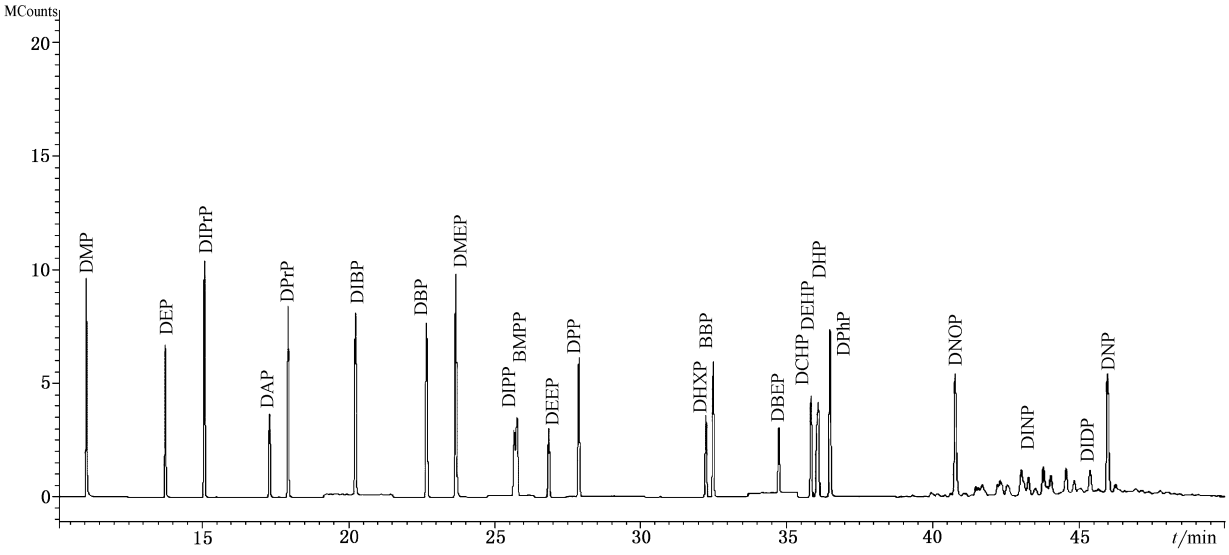


Figure C. 1 SIM gram of 23 phthalate esters by GC-MS

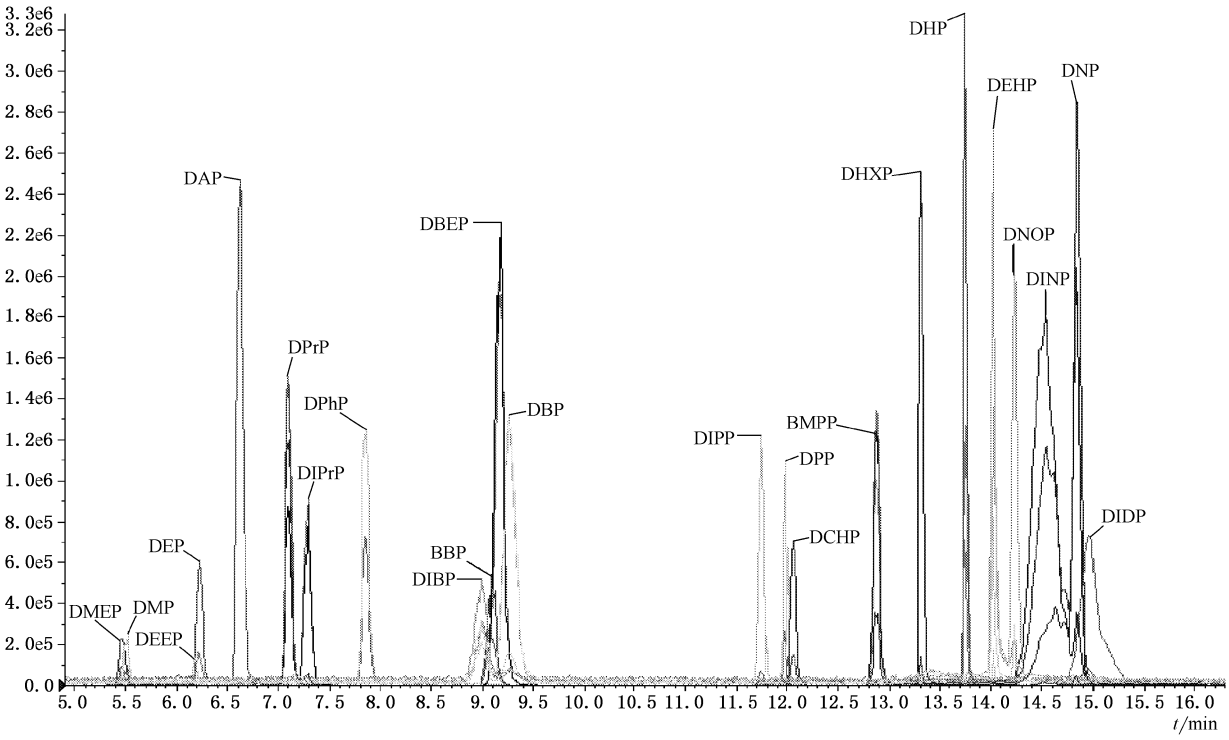


Figure C. 2 MRM gram of 23 phthalate esters by LC-MS/MS

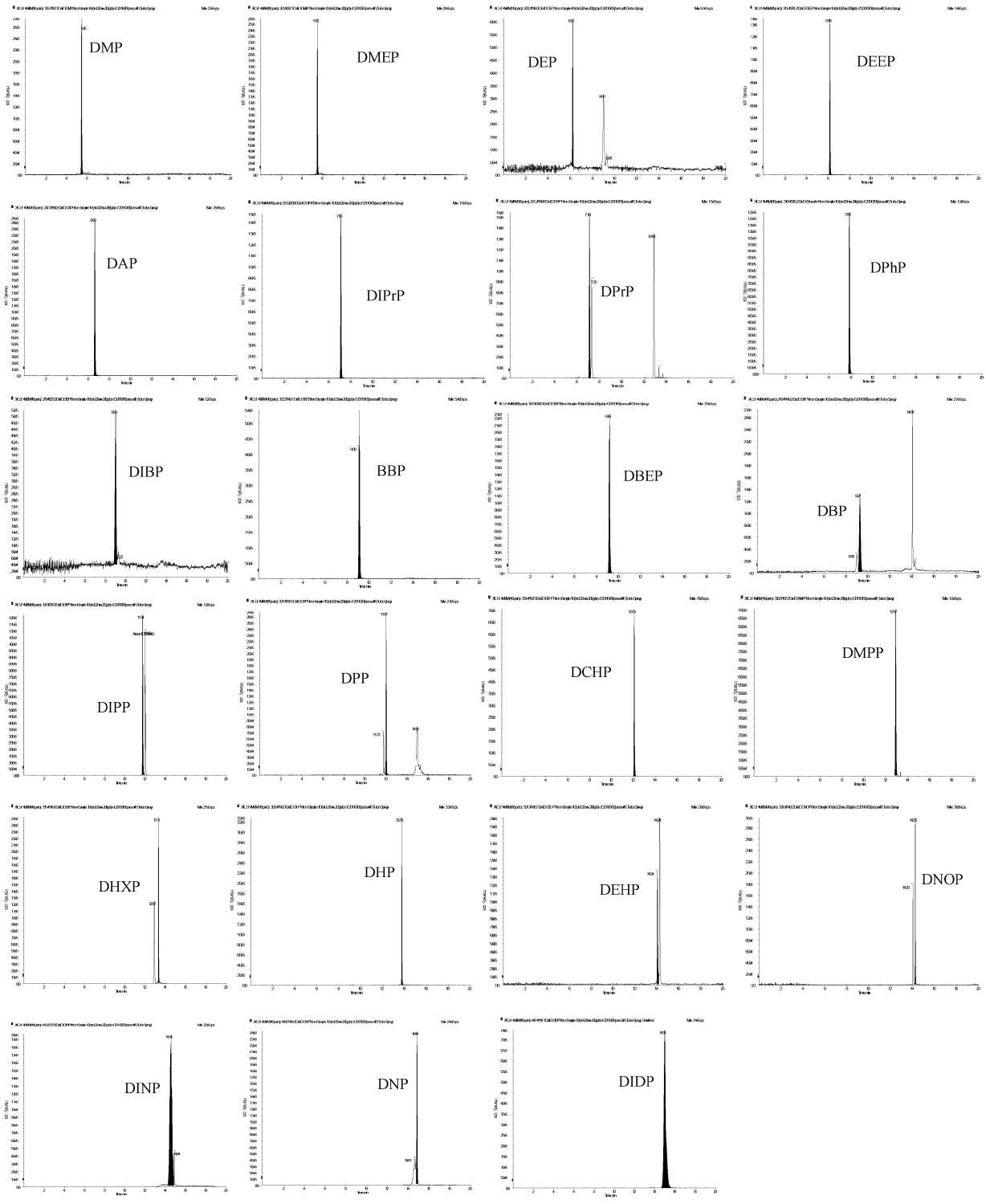


Figure C. 3 MRM gram of quantitation ion pair of 23 phthalate esters by LC-MS/MS

Annex D
(informative)
Recovery of 23 phthalic acid esters in various fortified concentrations

Table D. 1—Recovery of 23 phthalic acid esters in various fortified concentrations by GC-MS
(n = 6, average Recovery)

Compound	Spiked concentration mg/kg	Recovery/%									
		Guava juice	Solid lactic acid bacteria beverage	Seasoning powder	Grape jelly	lemon flavored	Fruit crisp	grapefruit sauce	egg noodles	olive oil	papaya milk
DMP	0. 1	89. 4	92. 1	82. 1	96. 9	102. 2	82. 9	82. 2	82. 1	82. 6	83. 3
	1. 0	98. 6	83. 3	93. 3	96. 2	101. 4	90. 3	95. 3	96. 8	99. 3	95. 3
	10. 0	92. 6	87. 6	89. 6	106. 2	99. 6	99. 6	89. 9	99. 6	99. 6	99. 6
DEP	0. 1	92. 1	97. 6	93. 6	98. 6	89. 8	98. 6	90. 6	100. 6	99. 6	95. 2
	1. 0	97. 7	97. 4	85. 4	99. 6	104. 2	95. 5	88. 4	86. 4	86. 4	86. 4
	10. 0	100. 2	86. 8	96. 8	92. 6	99. 8	93. 8	97. 8	98. 8	97. 8	97. 9
DIPrP	0. 1	91. 6	85. 7	94. 6	95. 2	98. 6	94. 2	90. 6	99. 4	94. 6	96. 4
	1. 0	98. 8	93. 6	92. 2	95. 4	95. 7	98. 2	99. 2	90. 2	94. 2	92. 2
	10. 0	95. 6	85. 4	96. 4	91. 6	91. 3	96. 6	96. 8	98. 4	90. 4	96. 4
DAP	0. 1	82. 4	93. 7	91. 6	98. 6	89. 8	95. 3	86. 3	82. 3	85. 8	88. 3
	1. 0	97. 6	102. 3	98. 8	95. 6	88. 2	92. 3	92. 4	82. 1	92. 4	92. 2
	10. 0	100. 7	93. 1	95. 6	94. 3	101. 2	89. 6	86. 6	92. 6	84. 6	85. 6
DPrP	0. 1	89. 5	97. 5	99. 5	101. 4	90. 6	89. 5	89. 4	89. 4	89. 9	89. 2
	1. 0	98. 5	88. 4	98. 3	96. 2	88. 4	88. 7	98. 8	98. 6	96. 5	96. 5
	10. 0	93. 6	104. 7	99. 6	96. 5	97. 8	96. 2	96. 6	92. 6	91. 6	94. 6
DIBP	0. 1	96. 3	87. 5	96. 9	81. 2	90. 6	92. 2	96. 0	92. 1	96. 6	98. 3
	1. 0	94. 7	97. 9	96. 2	95. 6	99. 2	98. 7	98. 7	97. 7	97. 7	94. 5
	10. 0	101. 2	92. 4	106. 2	108. 3	96. 8	100. 8	101. 4	100. 2	101. 6	101. 6
DBP	0. 1	93. 6	86. 8	98. 6	89. 4	86. 9	99. 1	98. 6	91. 6	92. 6	92. 6
	1. 0	98. 7	97. 7	99. 6	98. 8	101. 2	102. 6	95. 7	98. 8	98. 8	97. 7
	10. 0	92. 3	95. 7	92. 6	96. 6	100. 2	102. 5	91. 3	95. 6	91. 3	94. 8
DIPP	0. 1	93. 6	102. 0	98. 9	96. 0	102. 4	92. 6	89. 8	82. 4	95. 8	89. 8
	1. 0	95. 2	97. 3	96. 1	98. 7	102. 2	97. 7	88. 2	97. 6	99. 8	101. 2
	10. 0	89. 4	83. 3	96. 6	101. 4	95. 8	94. 8	101. 2	100. 7	100. 4	101. 1
DMEP	0. 1	95. 2	107. 0	98. 7	92. 4	80. 1	89. 8	82. 1	90. 2	98. 7	85. 9
	1. 0	103. 1	113. 1	95. 8	89. 8	96. 8	101. 2	85. 6	102. 3	95. 8	104. 4
	10. 0	92. 7	95. 4	96. 9	95. 8	99. 6	101. 1	95. 6	100. 6	96. 9	99. 9

Table D. 1（continued）

Compound	Spiked concentration mg/kg	Recovery/%									
		Guava juice	Solid lactic acid bacteria beverage	Seasoning powder	Grape jelly	lemon flavored	Fruit crisp	grapefruit sauce	egg noodles	olive oil	papaya milk
BMPP	0. 1	102. 2	87. 9	98. 8	95. 5	100. 6	98. 6	84. 7	100. 4	98. 8	98. 7
	1. 0	101. 4	93. 5	96. 8	92. 3	86. 4	95. 6	85. 8	101. 5	96. 8	105. 5
	10. 0	99. 6	91. 4	100. 4	99. 9	98. 8	94. 3	101. 1	96. 8	100. 4	102. 5
DEEP	0. 1	89. 8	94. 2	95. 8	92. 2	95. 2	81. 2	88. 9	85. 6	95. 8	89. 7
	1. 0	104. 2	97. 4	82. 8	98. 7	86. 4	85. 6	85. 6	96. 9	82. 8	101. 4
	10. 0	99. 8	94. 9	99. 6	100. 8	97. 9	86. 2	102. 5	100. 1	99. 6	101. 1
DPP	0. 1	92. 4	94. 1	102. 2	99. 1	96. 4	90. 1	92. 4	82. 2	102. 2	92. 9
	1. 0	101. 2	91. 4	96. 1	102. 6	92. 2	91. 2	89. 8	93. 3	96. 1	98. 8
	10. 0	96. 8	107. 4	100. 1	102. 5	96. 4	102	95. 8	96. 8	100. 1	93. 3
DHXP	0. 1	88. 8	86. 4	86. 3	93. 7	98. 6	102. 2	95. 5	86. 9	88. 8	98. 7
	1. 0	102. 2	97. 7	98. 5	102. 3	95. 7	94. 5	92. 3	101. 2	90. 9	91. 1
	10. 0	94. 4	98. 3	92. 1	93. 1	91. 3	103. 2	99. 9	100. 2	95. 5	100. 5
BBP	0. 1	88. 7	86. 2	88. 7	97. 5	89. 8	101. 4	96. 2	102. 4	98. 9	102. 1
	1. 0	94. 8	97. 2	94. 8	88. 4	88. 2	96. 2	102. 2	102. 2	102. 8	101. 1
	10. 0	92. 5	93. 6	92. 5	104. 7	101. 2	96. 5	96. 8	95. 8	100. 7	102. 2
DBEP	0. 1	98. 7	93. 4	88. 8	98. 8	98. 9	81. 2	102. 4	84. 5	82. 8	98. 7
	1. 0	92. 9	104. 7	90. 9	96. 8	104. 5	95. 6	110. 2	101. 4	101. 1	96. 8
	10. 0	100. 3	101. 2	95. 5	100. 4	99. 7	108. 3	81. 2	102. 8	101. 6	102. 8
DCHP	0. 1	93. 6	94. 6	98. 9	95. 8	89. 8	94. 3	100. 8	92. 2	98. 7	98. 9
	1. 0	102. 5	102. 5	102. 8	82. 8	106. 1	80. 9	97. 6	98. 7	98. 9	108. 2
	10. 0	93. 6	97. 4	100. 7	99. 6	100. 1	91. 4	100. 9	100. 8	99. 9	96. 8
DHP	0. 1	86. 3	96. 3	82. 8	95. 2	84. 7	91. 6	89. 8	99. 1	85. 8	101. 2
	1. 0	89. 7	99. 7	101. 1	86. 4	85. 8	88. 6	101. 4	102. 6	101. 4	96. 6
	10. 0	95. 6	85. 6	101. 6	97. 9	101. 1	88. 2	99. 4	102. 5	103. 3	94. 4
DEHP	0. 1	86. 9	92. 3	98. 7	96. 4	88. 9	87. 7	94. 1	98. 7	96. 8	88. 9
	1. 0	97. 8	95. 6	98. 9	92. 2	85. 6	94. 4	95. 8	100. 4	98. 3	92. 7
	10. 0	101. 2	86. 5	99. 9	96. 4	102. 5	96. 6	102. 2	101. 2	100. 5	96. 8
DPhP	0. 1	98. 7	87. 6	80. 1	89. 8	95. 5	95. 5	102. 1	102. 2	102. 4	99. 9
	1. 0	103. 2	93. 4	96. 8	104. 2	98. 2	98. 2	85. 5	101. 4	98. 7	91. 9
	10. 0	109. 3	98. 4	99. 6	99. 8	99. 6	99. 6	102. 5	99. 6	106. 6	104. 3
DNOP	0. 1	98. 2	83. 5	100. 6	92. 4	92. 4	92. 4	103. 4	89. 8	92. 4	95. 8
	1. 0	106. 3	102. 0	86. 4	101. 2	89. 6	89. 6	92. 5	104. 2	106. 2	99. 1
	10. 0	98. 7	98. 7	98. 8	96. 8	109. 6	101. 6	104. 5	99. 8	99. 6	100. 4

Table D. 1（continued）

Compound	Spiked concentration mg/kg	Recovery/%									
		Guava juice	Solid lactic acid bacteria beverage	Seasoning powder	Grape jelly	lemon flavored	Fruit crisp	grapefruit sauce	egg noodles	olive oil	papaya milk
DINP	0. 5	93. 6	109. 6	103. 4	96. 8	84. 4	88. 8	84. 8	84. 8	96. 8	104. 8
	1. 0	94. 7	83. 2	99. 4	84. 5	86. 9	82. 6	98. 7	92. 4	95. 2	98. 9
	10. 0	98. 5	94. 7	98. 4	102. 8	100. 2	92. 2	92. 1	96. 8	98. 7	99. 7
DIDP	0. 5	86. 6	93. 6	89. 8	97. 4	82. 8	104. 4	100. 8	101. 4	91. 2	85. 4
	1. 0	96. 8	89. 8	82. 3	92. 2	102. 4	97. 7	104. 2	88. 8	92. 1	89. 8
	10. 0	103. 6	87. 4	92. 6	100. 8	95. 8	92. 5	100. 1	94. 4	95. 8	100. 1
DNP	0. 1	79. 6	89. 6	78. 6	102. 3	105. 6	98. 6	89. 3	78. 6	80. 2	90. 3
	1. 0	102. 3	95. 3	89. 3	120. 3	89. 6	98. 6	92. 3	106. 3	106. 8	102. 3
	10. 0	89. 6	89. 2	103. 6	112. 6	98. 3	85. 3	89. 6	103. 6	98. 6	104. 3

Table D. 2—Recovery of 23 phthalic acid esters in various fortified concentrations by LC-MS/MS（n = 6，average Recovery）

Compound	Spiked concentration mg/kg	Recovery/%									
		Guava juice	Solid lactic acid bacteria beverage	Seasoning powder	Grape jelly	lemon flavored	Fruit crisp	grapefruit sauce	egg noodles	olive oil	papaya milk
DMP	0. 1	98. 1	92. 8	92. 8	89. 5	96. 6	84. 1	94. 6	89. 6	92. 1	97. 6
	1	98. 2	97. 1	97. 1	112	81. 9	90. 3	91. 9	109	93. 7	91. 1
	10	97. 7	92. 15	92. 15	103	102	99. 6	93. 4	96. 4	99. 6	93. 4
DEP	0. 1	97. 4	84. 2	84. 2	83. 5	98. 7	94. 3	88. 7	89. 7	93. 6	89. 7
	1	97. 8	97. 2	97. 2	89. 8	83. 5	86. 2	88. 5	98. 5	85. 4	98. 5
	10	97. 89	97. 81	97. 81	91. 1	95. 4	99. 8	97. 4	97. 2	98. 8	97. 2
DIPrP	0. 1	99. 3	79. 5	79. 5	78. 8	85. 7	99. 6	95. 7	95. 7	99. 6	95. 7
	1	107. 8	101. 1	101. 1	94. 6	92. 8	90. 2	92. 9	92. 9	91. 2	92. 9
	10	100. 1	101. 1	101. 1	95. 1	101	100. 4	100	100	86. 4	100
DAP	0. 01	93. 2	97. 3	97. 3	97. 8	81. 3	86. 5	91. 3	91. 3	96. 5	91. 3
	0. 05	92. 2	86. 4	86. 4	99. 4	80. 6	84. 2	81	81	82. 2	81
	1	99. 8	89. 8	89. 8	98. 1	98. 1	94. 3	93. 1	93. 1	94. 6	93. 1
DPrP	0. 1	95. 2	75. 5	75. 5	76. 9	89. 2	97. 7	89. 2	89. 6	99. 5	89. 6
	1	96. 8	86. 8	86. 8	101	79. 8	92. 5	99. 8	109	99. 1	109
	10	97. 8	91. 23	91. 23	101	96. 4	94. 6	96. 4	96. 4	83. 6	96. 4
DIBP	0. 1	97. 2	93. 8	93. 8	83. 7	98	96. 3	98	98	96. 3	98
	1	97. 8	91. 3	91. 3	94. 5	93. 6	98. 7	96. 6	98. 5	94. 7	96. 6
	10	94. 89	94. 11	94. 11	92. 1	95. 1	104. 2	94. 2	97. 2	101. 2	94. 2

Table D. 2（continued）

Compound	Spiked concentration mg/kg	Recovery/%									
		Guava juice	Solid lactic acid bacteria beverage	Seasoning powder	Grape jelly	lemon flavored	Fruit crisp	grapefruit sauce	egg noodles	olive oil	papaya milk
DBP	0. 1	92. 3	87. 7	87. 7	82. 7	98. 7	95. 6	96. 7	76. 7	93. 6	76. 7
	1	94. 8	91. 8	91. 8	94. 8	94. 5	98. 6	94. 1	84. 1	94. 7	84. 1
	10	102. 1	103. 3	103. 3	102. 1	104	97. 3	103	105	101. 4	105
DIPP	0. 1	93. 3	83. 5	83. 5	93. 6	115	97. 7	114	91. 4	91. 9	114
	1	95. 8	91. 8	91. 8	98. 5	111	97. 8	111	111	96. 1	111
	10	100. 2	101. 2	101. 2	92. 2	94. 3	108. 4	94. 3	94. 3	86. 6	94. 3
DMEP	0. 1	98. 3	98. 7	98. 7	95	91. 4	97. 7	91. 4	114	95. 2	91. 4
	1	93. 8	112	112	105. 4	112	96. 8	112	110. 5	96. 4	112
	10	92. 28	101. 2	101. 2	100. 2	101. 2	93. 9	101. 2	101. 2	95. 6	101. 2
BMPP	0. 1	93. 8	95. 4	95. 4	96. 7	95. 4	98. 9	95. 4	95. 4	91. 6	95. 4
	1	95. 3	92. 3	92. 3	92. 3	92. 3	96. 1	92. 3	92. 3	95. 6	92. 3
	10	92. 28	92. 38	92. 38	92. 3	92. 4	102. 4	92. 4	92. 4	84. 3	92. 4
DEEP	0. 1	93. 5	98. 1	98. 1	94. 4	98. 6	95. 8	98. 6	98. 6	87. 2	98. 6
	1	91. 3	91. 2	91. 2	81. 2	91. 2	82. 8	91. 2	91. 2	95. 6	91. 2
	10	91. 23	91. 21	91. 21	98. 2	91. 2	99. 6	91. 2	91. 2	86. 2	91. 2
DPP	0. 1	93. 6	93. 6	93. 6	91. 8	91. 6	101. 2	91. 6	91. 6	94. 1	91. 6
	1	94. 6	84. 5	84. 5	83. 1	83. 1	96. 7	83. 1	83. 1	91. 2	83. 1
	10	95. 24	85. 24	85. 24	83. 3	83. 3	109. 1	83. 3	83. 3	102	83. 3
DHXP	0. 1	99. 1	91. 9	91. 9	83. 6	88. 5	89. 8	88. 7	88. 7	102. 2	88. 7
	1	95. 9	95. 9	95. 9	91. 4	91. 9	93. 9	91. 4	91. 4	92. 5	91. 4
	10	98. 71	91. 71	91. 71	91. 5	91. 7	96. 5	91. 7	91. 7	101. 2	91. 7
BBP	0. 1	94. 9	94. 9	94. 9	93. 5	84. 6	98. 9	84. 6	79. 6	94. 5	84. 6
	1	112. 1	112. 3	112. 3	97. 1	97. 1	101. 8	97. 1	97. 1	101. 1	97. 1
	10	98. 99	98. 91	98. 91	99. 5	98. 1	98. 7	98. 1	98. 1	103. 8	98. 1
DBEP	0. 1	94. 5	97. 7	97. 7	93. 5	93. 5	87. 8	93. 5	93. 5	97. 2	93. 5
	1	112. 1	111. 1	111. 1	112	112. 1	101. 1	112. 1	112. 1	97. 7	112. 1
	10	98. 99	100. 2	100. 2	91	91	101. 2	91	91	101. 8	91
DCHP	0. 1	93. 7	98. 3	98. 3	92. 8	92. 5	98. 7	92. 5	92. 5	93. 1	92. 5
	1	102. 1	110. 1	110. 1	94. 37	110	97. 9	110	110	101. 2	110
	10	98. 21	98. 21	98. 21	97. 3	97. 21	91. 9	97. 21	97. 21	107. 5	97. 21
DHP	0. 1	98. 8	89. 6	89. 6	87. 2	79	88. 8	79	79	98. 1	79
	1	103. 2	103. 1	103. 1	115	114. 1	102. 4	115. 2	113. 1	101. 4	112. 1
	10	98. 24	91. 24	91. 24	96. 5	99. 91	93. 3	99. 91	99. 91	100. 2	99. 91

Table D. 2（continued）

Compound	Spiked concentration mg/kg	Recovery/%									
		Guava juice	Solid lactic acid bacteria beverage	Seasoning powder	Grape jelly	lemon flavored	Fruit crisp	grapefruit sauce	egg noodles	olive oil	papaya milk
DEHP	0. 1	93. 9	92. 8	92. 8	81. 6	81	97. 8	81	81	101. 3	81
	1	98. 1	92. 1	92. 1	91. 1	93. 1	98. 8	93. 1	93. 1	107. 4	93. 1
	10	98. 5	97. 5	97. 5	91. 8	92. 91	102. 5	92. 91	92. 91	99. 9	92. 91
DPhP	0. 1	94. 6	103	103	94. 9	90. 3	104. 4	89. 1	89. 1	87. 8	89. 1
	1	99. 3	94. 1	94. 1	112	102. 3	91. 7	102. 3	102. 3	103. 2	102. 3
	10	99. 12	99. 3	99. 3	94. 3	93. 31	107. 6	93. 31	93. 31	99. 3	93. 31
DNOP	0. 1	92	91. 7	91. 7	91. 4	94	96. 3	94. 4	94. 6	99. 4	94. 6
	1	99. 6	96. 7	96. 7	95. 6	94. 7	101. 2	94. 7	94. 7	89. 1	94. 7
	10	99. 79	102. 1	102. 1	105	103. 1	96. 6	103. 1	103. 1	101. 6	103. 1
DINP	0. 1	103. 4	83. 6	83. 6	83	106	102. 8	90	90	90. 8	95
	1	97. 6	87. 8	87. 8	91. 4	98	99. 9	98	98	92. 6	98
	10	99. 89	91. 9	91. 9	86. 1	100. 1	98. 7	100. 1	100. 1	97. 2	100. 1
DIDP	0. 1	91. 4	87. 2	87. 2	102	98	84. 4	99. 2	89. 2	102. 4	99. 2
	1	109	99. 6	99. 6	95. 6	93	99. 8	93. 5	95. 5	98. 7	93. 5
	10	99. 6	99. 2	99. 2	99. 4	99. 6	100. 1	99. 1	99. 1	102. 5	99. 1
DNP	0. 1	110. 3	102. 3	89. 7	96. 3	98. 5	96. 3	98. 3	102. 9	112. 6	87. 9
	1	98. 6	101. 2	98. 6	89. 6	103. 6	88. 9	78. 9	86. 9	86. 3	84. 9
	10	88. 9	99. 6	102. 3	111. 9	89. 9	96. 3	98. 6	99. 1	103. 6	89. 9