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中华人民共和国出入境检验检疫行业标准

SN/T 3235—2012

出口动物源食品中多类禁用药物残留量检测方法　液相色谱-质谱/质谱法

Determination of multi-groups of banned drug residues in foodstuffs of animal origin for export—LC-MS/MS method

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前　言

本标准按照 GB/T 1.1—2009 给出的规则起草。

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：中华人民共和国深圳出入境检验检疫局、中华人民共和国上海出入境检验检疫局、深圳大学。

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1　范围

本标准规定了动物源性食品中包括β-受体激动剂类、雄性激素类、雌性激素类、糖皮质激素类、硝基咪唑类、二羟基苯甲酸内酯类、三苯甲烷类、镇静剂类以及氯霉素等九类禁用药物残留量测定的制样、液相色谱-质谱/质谱筛查和测定。多种禁用兽药标准品信息参见附录A。

本标准适用于牛奶、动物肌肉中西玛特罗、克仑特罗、菲诺特罗、莱克多巴胺、沙丁胺醇、特布他林、妥布特罗、去氢睾酮、表睾酮、去氢甲睾酮、诺龙、睾酮、丙酸倍氯米松、倍他米松、曲安西龙、曲安奈德、玉米赤霉烯酮、α-玉米赤霉烯醇、β-玉米赤霉烯醇、玉米赤霉酮、α-玉米赤霉醇、β-玉米赤霉醇、地美硝唑、异丙硝唑、甲硝唑、洛硝哒唑、己二烯雌酚、己烯雌酚、己烷雌酚、氯西嗪、地西泮及氯霉素的筛查和测定。

本标准适用于肝脏中西玛特罗、克仑特罗、莱克多巴胺、沙丁胺醇、特布他林、妥布特罗、去氢睾酮、表睾酮、甲睾酮、诺龙、睾酮、倍他米松、氢化可的松、曲安西龙、曲安奈德、玉米赤霉烯酮、α-玉米赤霉烯醇、β-玉米赤霉烯醇、玉米赤霉酮、α-玉米赤霉醇、β-玉米赤霉醇、地美硝唑、异丙硝唑、甲硝唑、洛硝哒唑、己二烯雌酚、己烯雌酚、己烷雌酚、氯丙嗪、地西泮及氯霉素的筛查和测定。

本标准适用于水产品中西玛特罗、克仑特罗、菲诺特罗、莱克多巴胺、沙丁胺醇、特布他林、妥布特罗、去氢睾酮、表睾酮、氟甲睾酮、去氢甲睾酮、甲睾酮、丙酸诺龙、诺龙、丙酸睾酮、睾酮、丙酸倍氯米松、倍他米松、醋酸可的松、氟氢可的松、氢化可的松、曲安西龙、曲安奈德、玉米赤霉烯酮、α-玉米赤霉烯醇、β-玉米赤霉烯醇、玉米赤霉酮、α-玉米赤霉醇、β-玉米赤霉醇、地美硝唑、异丙硝唑、甲硝唑、洛硝哒唑、羟甲基甲硝咪唑、己二烯雌酚、己烯雌酚、己烷雌酚、氯丙嗪、地西泮、氯霉素、孔雀石绿、隐性孔雀石绿、结晶紫及隐性结晶紫的筛查和测定。

2　规范性引用文件

下列文件对于本文件的应用是必不可少的。凡是注日期的引用文件，仅注日期的版本适用于本文件。凡是不注日期的引用文件，其最新版本(包括所有的修改单)适用于本文件。

GB/T 6682　分析实验室用水规格和试验方法

3　样品制备与保存

3.1　动物肝脏、肌肉和水产品

从所取全部样品中取出有代表性样品可食部分约500 g，用组织捣碎机充分捣碎均匀，装入洁净容器中，密封，并标明标记，于−18 ℃以下冷冻存放。

3.2　牛奶

从所取全部样品中取出有代表性样品500 mL，充分混匀，装入洁净容器中，密封，并标明标记，于−18 ℃以下冷冻存放。

4 方法提要

对于水产品中的禁用药物，分别以氨化乙腈和酸化乙腈提取；对于牛奶、肝脏和肌肉中的禁用药物，用β-葡糖苷醛甙酶-芳基硫酸酯酶在乙酸铵缓冲液中酶解后，分别以氨化乙腈和酸化乙腈提取。提取液以 QuEChERS 吸附剂净化后，用高效液相色谱-质谱/质谱仪测定，内标法或外标法定量。

5 试剂和材料

除另有规定外，所有试剂均为分析纯；水为 GB/T 6682 规定的一级水。

5.1 乙腈，色谱级。

5.2 甲醇，色谱级。

5.3 冰乙酸，色谱级。

5.4 氨水，色谱级。

5.5 乙酸铵，色谱级。

5.6 甲酸，色谱纯。

5.7 β-葡糖苷醛甙酶-芳基硫酸酯酶，含 β-盐酸葡萄糖醛甙酶 134 600 U/mL，芳基硫酸酯酶 5 200 U/mL。

5.8 N-丙基乙二胺吸附剂(PSA)，40 μm～60 μm 粒径范围，100 Å 平均孔径。

5.9 十八烷基键合硅胶吸附剂(C_{18}-封端)，40 μm～60 μm 粒径范围，60 Å 平均孔径。

5.10 石墨化碳黑吸附剂(GCB)，40μm～60μm 粒径范围，60 Å 平均孔径。

5.11 无水硫酸钠，分析纯，500 ℃灼烧 4 h，置于干燥器中备用。

5.12 无水硫酸镁，分析纯，500 ℃灼烧 4 h，置于干燥器中备用。

5.13 乙酸铵缓冲溶液：溶解 7.7 g 乙酸铵(5.5)于 480 mL 水中，用冰乙酸(5.3)调节溶液 pH 值到 5.2，以水定容至 500 mL。

5.14 1%氨水-乙腈溶液：准确吸取 40 mL 25%的氨水(5.4)至 1 000 mL 容量瓶，用乙腈(5.1)定容至刻度，混匀。

5.15 1%乙酸-乙腈溶液：准确吸取 10 mL 冰乙酸(5.3)至 1 000 mL 容量瓶，用乙腈(5.1)定容至刻度，混匀。

5.16 20%的乙腈-水溶液：准确吸取 10 mL 乙腈(5.1)，加入 90 mL 水，混匀。

5.17 色谱流动相 1，0.1%甲酸-水溶液：取 1 mL 甲酸(5.6)用去离子水定容到 1 000 mL，混匀。

5.18 色谱流动相 2，0.1%甲酸-甲醇溶液：取 1 mL 甲酸(5.6)用甲醇(5.2)定容到 1 000 mL，混匀。

5.19 QuEChERS 吸附剂 1(适用于猪肝和动物组织样品)：准确称取 100 mg PSA(5.8)、50 mgC_{18}(5.9)、20 mg GCB(5.10)和 400 mg 无水 $MgSO_4$(5.12)，储存于 25 mL 具螺旋盖聚丙烯离心管中，旋紧管盖，置于干燥箱内备用。

5.20 QuEChERS 吸附剂 2(适用于牛奶、水产品样品)：准确称取 100 mg PSA、40 mg C_{18}和 600 mg 无水 $MgSO_4$，储存于 25 mL 具螺旋盖聚丙烯离心管中，旋紧管盖，置于干燥箱内备用。

5.21 标准物质：β-受体激动剂类、雄性激素类、糖皮质激素类、雌性激素类、硝基咪唑类、镇静剂类、二羟基苯甲酸内酯类、三苯甲烷类以及氯霉素标准物质的纯度均≥99%，参见附录 A 表 A.1。

5.22 D_3-沙丁胺醇、D_5-氯丙嗪、D_5-莱克多巴胺、D_6-隐性结晶紫、D_5-孔雀石绿、D_9-克仑特罗、D_3-洛硝唑、D_6-结晶紫、D_6-隐性孔雀石绿、D_8-己二烯雌酚及 D_5-氯霉素的标准物质的纯度均≥95%。

5.23 标准贮备液：准确称取 10.0 mg 按其纯度折算为 100%质量的各个化合物的标准物质(5.21)，甲醇溶解定容至 10.0 mL，溶液浓度相当于 100.0 mg/L，－30 ℃冷冻保存，有效期为 12 个月。

5.24 标准中间溶液：准确吸取 1.0 mL 各标准贮备溶液(5.23)，以甲醇稀释并定容于 100 mL 棕色容

量瓶，浓度相当于 1.0 mg/L，4 ℃冷藏保存，有效期为 6 个月。

5.25 空白基质溶液：选取不含待测物的样品，按照 7.1 和 7.2 步骤操作，得到空白基质溶液。

5.26 基质混合标准溶液：根据需要用空白基质溶液(5.25)稀释标准中间溶液(5.24)成适合浓度的混合标准工作溶液，现配现用。

5.27 内标贮备液：准确称取 10.0 mg 按其纯度折算为 100%质量的内标标准物质(5.22)，以甲醇溶解并定容于 10 mL 棕色容量瓶，浓度相当于 100.0 mg/L，−30 ℃冷冻保存，有效期为 12 个月。

5.28 内标中间溶液：准确吸取 1 mL 各内标贮备溶液(5.26)，以甲醇稀释并定容于 100 mL 棕色容量瓶，浓度相当于 1.0 mg/L，4 ℃冷藏保存，有效期为 6 个月。

5.29 内标工作液：根据需要用空白基质溶液(5.25)稀释内标中间溶液(5.28)成合适浓度的标准内标工作溶液，现配现用。

5.30 微孔滤膜：0.22 μm，水相和有机相型。

6 仪器和设备

6.1 高效液相色谱四级杆质谱/质谱仪：配有电喷雾离子源。

6.2 电子分析天平：感量 0.1 mg，0.01 g。

6.3 减压旋转蒸发仪。

6.4 旋涡混合器。

6.5 高速冷冻离心机：最大转速为 10 000 r/min。

6.6 微量移液器：量程 10 μL～100 μL，100 μL～1 000 μL。

6.7 pH 计。

6.8 螺旋盖聚丙烯离心试管，50 mL。

6.9 组织捣碎机。

6.10 恒温水浴振荡器。

6.11 平板振荡器。

7 测定步骤

7.1 样品提取

7.1.1 牛奶和动物组织(肝脏、肌肉等)

称取试样 2 g(精确到 0.01 g)，置于 50 mL 具螺旋盖聚丙烯离心管中，准确加入 20 μL 内标工作液(5.29)，8 mL 乙酸铵缓冲液(5.13)，在均质器中高速均质 30 s，加入 30 μL β-葡糖苷醛甙酶-芳基硫酸酯酶(5.7)，涡旋混匀 30 s，37 ℃振荡温育 12 h。取出样品静置，使其温度降至室温。加入 15 mL 1%氨水-乙腈溶液(5.14)，5.0 g 无水硫酸钠(5.11)，涡旋混匀 1 min 后，在 4 ℃、9 500 r/min 离心 5 min，收集上清液于另一 50 mL 离心管。剩余部分重新加入 15 mL 1%乙酸-乙腈溶液(5.15)，旋紧螺旋盖，室温下平置于水平振荡器，振荡提取 10 min，在 4 ℃、9 500 r/min 离心 5 min，吸取上清液层溶液，合并两次提取有机相，待净化。

7.1.2 水产品(鱼)

称取试样 2 g(精确到 0.01 g)，置于 50 mL 具螺旋盖聚丙烯离心管中，准确加入 20 μL 内标工作液(5.29)，8 mL 乙酸铵缓冲液(5.13)，高速涡旋混匀 30 s，室温静置 30 min。加入 15 mL 1%氨水-乙腈溶液(5.14)，5.0 g 无水硫酸钠(5.11)，涡旋混匀 1 min 后，在 4 ℃、9 500 r/min 离心 5 min。收集上清

液于另一个干净的 50 mL 具螺旋盖离心管中。剩余混合物中加入 15 mL 1%乙酸-乙腈溶液(5.15),旋紧螺旋盖,室温置于水平振荡器,振荡提取 10 min,在 4 ℃、9 500 r/min 下离心 5min,吸取上清液层溶液,合并两次提取有机相,待净化。

7.2 净化

一次性全部将 QuEChERS 吸附剂 1 加入肝脏或肌肉样品的提取液中,或将 QuEChERS 吸附剂 2 加入牛奶、水产品提取液中,旋紧螺旋盖,高速涡旋 1 min,在 4 ℃、于 9 500 r/min 离心 5 min。吸取所有有机相溶液,在减压旋转蒸发装置上于 42 ℃蒸发至近干。加入 2.0 mL 的 10%乙腈-水溶液(5.16)溶解残渣,涡旋混合 1 min,过 0.22 μm 滤膜(5.30)。滤液供液相色谱-质谱/质谱仪测定。

7.3 测定

7.3.1 液相色谱条件

7.3.1.1 色谱柱:C_{18}柱,150 mm×2.1 mm(内径),粒径 3.0 μm 或相当者。

7.3.1.2 流动相:A1:含 0.1%甲酸的水溶液(5.17),B1:含 0.1%甲酸-甲醇溶液(5.18);A2:水,B2:乙腈。

7.3.1.3 流速:250 μL/min。

7.3.1.4 柱温:35 ℃。

7.3.1.5 进样量:10 μL。

7.3.1.6 梯度洗脱程序见表 1。

表 1 液相色谱梯度洗脱程序表

正离子模式(ESI⁺)			负离子模式(ESI⁻)		
时间 min	A1 %	B1 %	时间 min	A2 %	B2 %
0.00	95.0	5.0	0.00	80.0	20.0
4.00	45.0	55.0	8.00	2.0	98.0
5.00	5.0	95.0	9.00	2.0	98.0
8.00	5.0	95.0	10.00	80.0	20.0
13.00	95.0	5.0	18.00	80.0	20.0
22.00	95.0	5.0			

7.3.2 质谱条件

7.3.2.1 离子源:电喷雾 ESI,正/负离子模式。

7.3.2.2 扫描方式:多反应监测 MRM(锁定保留时间)。

7.3.2.3 雾化气压力(GS1)、气帘气压力(CUR)、辅助气流速(GS2)均为高纯氮气或其他合适气体;使用前应调节各气体流量以及离子源温度(TEM)使质谱灵敏度达到检测要求,质谱等详细条件参见表 B.1。

7.3.2.4 电喷雾电压(IS)、碰撞电压(CE)、去簇电压(DP)、碰撞室入口电压(EP)、碰撞室出口电压(CXP)应优化至最佳灵敏度。监测离子对和定量离子等详细仪器条件参见表 C.1。

7.3.3 液相色谱-质谱/质谱测定

根据试样中被测物的药物含量,选取响应值相近的混合标准工作液(5.25)同时进行分析。混合标

准工作液和待测液中各种药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，应用甲醇：水(1/9，体积比)稀释到合适浓度后分析。在上述仪器条件下，44 种化合物的总离子流色谱图参见图 D.1，标准溶液中待测药物的多反应监测色谱图参见图 D.2，参考保留时间参见表 C.1。

7.4 空白实验

除不加试样外，均按上述操作步骤进行。

8 结果计算和表述

8.1 定性标准

8.1.1 保留时间

待测样品中化合物色谱峰的保留时间与标准溶液相比变化范围应在±2.5%之内。

8.1.2 定量离子、定性离子及子离子丰度比

每种化合物的质谱定性离子必须出现，至少应包括一个母离子和两个子离子，而且同一检测批次，对同一化合物，样品中目标化合物的两个子离子的相对丰度比与浓度相当的标准溶液相比，其允许偏差不超过表 2 规定的范围。

表 2 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/%	±20	±25	±30	±50

8.2 定量结果与表述

采用标准曲线法定量，按式(1)或仪器数据处理系统计算所有禁用药物的残留含量，计算结果需扣除空白值。

$$X=\frac{c\times V}{m}\times\frac{1\,000}{1\,000} \qquad \cdots\cdots(1)$$

式中：

X ——试样中待测组分的含量，单位为微克每千克(μg/kg)；

c ——待测组分响应值在标准曲线上计算得到的浓度，单位为微克每升(μg/L)；

V ——样品定容体积，单位为毫升(mL)；

m ——样品称样量，单位为克(g)。

9 测定低限和回收率

9.1 测定低限(LOQ)

本方法牛奶、猪肝、鸡肉、猪肉、鱼肉中的测定低限，参见表 E.1～表 E.5。

9.2 回收率

在不同的基质中，各化合物添加回收率范围的实验数据参见表 F.1～表 F.5。

附 录 A
（资料性附录）
多种禁用兽药标准品信息

表 A.1 多种碱性兽药标准品信息

英文名称	中文名称	CAS 号	结构式	相对分子质量
β-受体激动剂类(8 种)				
clenbuterol	克仑特罗	37148-27-9	$C_{12}H_{18}Cl_2N_2O$	277.19
salbutamol	沙丁胺醇	18559-94-9	$C_{13}H_{21}NO_3$	239.31
ractopamine	莱克多巴胺	97825-25-7	$C_{18}H_{23}NO_3$	301.38
cimaterol	西玛特罗	54239-37-1	$C_{12}H_{17}N_3O$	219.28
terbutaline	特布他林	23031-25-6	$C_{12}H_{19}NO_3$	225.29
tulobuterol	妥布特罗	41570-61-0	$C_{12}H_{18}ClNO$	227.73
fenoterol	菲诺特罗	13392-18-2	$C_{17}H_{21}NO_4$	303.35
雄性激素类(10 种)				
boldenone	去氢睾酮	846-48-0	$C_{19}H_{26}O_2$	286.41
testosterone propionate	丙酸睾酮	57-85-2	$C_{22}H_{32}O_3$	344.49
dehydro-17a-methyltestrosterone	去氢甲睾酮	72-63-9	$C_{20}H_{28}O_2$	300.44
methyltestosterone	甲睾酮	58-18-4	$C_{20}H_{30}O_2$	302.45
testostrone	睾酮	58-22-0	$C_{19}H_{28}O_2$	288.43
nandrolone 17-propionate	丙酸诺龙	7207-92-3	$C_{21}H_{30}O_3$	330.46
epiandrosterone	表睾酮	481-30-1	$C_{19}H_{28}O_2$	288.42
fluoxymesterone	氟甲睾酮	76-43-7	$C_{20}H_{29}FO$	336.44
nandrolone	诺龙	434-22-0	$C_{18}H_{26}O_2$	274.40
nandrolone phenylpropionate	苯丙酸诺龙	62-90-8	$C_{27}H_{34}O_3$	406.56
糖皮质激素类(7 种)				
betamethasone	倍他米松	378-44-9	$C_{22}H_{29}FO_5$	392.45
cortisone acetate	醋酸可的松	50-04-4	$C_{23}H_{30}O_6$	402.49
beclomethasone dipropionate	丙酸倍氯米松	4419-39-0	$C_{22}H_{29}ClO_5$	408.92
fludrocortisone	氟氢可的松	127-31-1	$C_{21}H_{29}FO_5$	380.453
hydrocortisone	氢化可的松	50-23-7	$C_{21}H_{30}O_5$	362.47
triamicinolone	曲安西龙	124-94-7	$C_{21}H_{27}FO_6$	394.44
triamcinolone acetonide	曲安奈德	76-25-5	$C_{24}H_{31}FO_6$	434.5
雌性激素类(3 种)				
diethylstilbestrol	己烯雌酚	56-53-1	$C_{18}H_{20}O_2$	268.35
hexestrol	己烷雌酚	84-16-2	$C_{18}H_{22}O_2$	270.37
dienestrol	己二烯雌酚	84-17-3	$C_{18}H_{18}O_2$	266.33

表 A.1（续）

英文名称	中文名称	CAS号	结构式	相对分子质量
硝基咪唑类(5种)				
1-methyl-5-nitro-1*H*-imidazole (HMMNI)	羟甲基甲硝咪唑	936-05-0	$C_5H_7N_3O_3$	157.13
dimetronidazole	地美硝唑	551-92-8	$C_5H_7N_3O_2$	157.13
ronidazole	洛硝哒唑	7681-76-7	$C_6H_8N_4O_4$	200.15
metronidazole	甲硝唑	443-48-1	$C_6H_9N_3O_3$	171.15
ipronidazole	异丙硝唑	14885-29-1	$C_7H_{11}N_3O_2$	169.18
二羟基苯甲酸内酯类(6种)				
α-zeranol	α-玉米赤霉醇	26538-44-3	$C_{18}H_{26}O_5$	322.4
β-zeranol	β-玉米赤霉醇	26538-44-3	$C_{18}H_{26}O_5$	322.4
α-zearalenol	α-玉米赤霉烯醇	36455-72-8	$C_{18}H_{24}O_5$	320.38
β-zearalenol	β-玉米赤霉烯醇	71030-11-0	$C_{18}H_{24}O_5$	320.38
zearalanone	玉米赤霉酮	5975-78-0	$C_{18}H_{24}O_5$	320.38
zearalenone	玉米赤霉烯酮	17924-92-4	$C_{18}H_{22}O_5$	318.36
三苯甲烷类(4种)				
malachite green	孔雀石绿	510-13-4	$C_{23}H_{26}N_2O$	346.46
leuco malachite green	隐性孔雀石绿	129-73-7	$C_{23}H_{26}N_2$	330.47
crystal violet	结晶紫	548-62-9	$C_{25}H_{30}N_3Cl$	407.98
leuco crystal violet	隐性结晶紫	603-48-5	$C_{25}H_{31}N_3$	373.53
镇静剂类(2种)				
chlorpromazine	氯丙嗪	50-53-3	$C_{17}H_{19}ClN_2S$	318.86
diazapam	地西泮	439-14-5	$C_{16}H_{13}ClN_2O$	284.74
氯霉素				
chloramphenicol	氯霉素	439-14-5	$C_{11}H_{12}C_{12}N_2O_5$	323.13

附 录 B
（资料性附录）
API 5000 型质谱/质谱仪参考质谱条件

表 B.1 API 5000 型质谱/质谱仪参考质谱条件

参考质谱条件	正离子模式(ESI$^+$)	负离子模式(ESI$^-$)
离子喷雾电压	4 500 V	−4 500 V
气帘气压力	1.7 bar	1.7 bar
雾化气压力	3.4 bar	3.4 bar
辅助气压力	4.4 bar	4.1 bar
离子源温度	450 ℃	500 ℃

附 录 C
（资料性附录）
多种禁用药物及其内标物的主要参考质谱参数

表 C.1 多种禁用药物及其内标物的主要参考质谱参数

化合物[a]	离子对 Q1/Q3(m/z)	保留时间 min	去簇电压(DP)/V	碰撞气能量(CE)/eV	碰撞室出口电压(CXP)/V	内标物
ESI^+模式						
丙酸倍氯米松 beclomethasone diptopionate	521.4/503[b]	12.7	51	37	12	
	521.4/337.2		51	71	4	
倍他米松 betanethasone	393.1/373.2[b]	11.3	41	33	18	
	393.1/355.2		41	31	8	
去氢睾酮 boldenone	287.6/120.9[b]	11.5	31	29	14	
	287.6/134.9		51	33	10	
氯丙嗪 chlorpromazine	319.1/86.1[b]	10.9	56	65	16	D_5-氯丙嗪
	319.1/58.2		56	37	12	
西玛特罗 cimaterol	220/160.1[b]	6.3	41	31	8	
	220/202.1		41	29	6	
克仑特罗 clentuterol	276.9/202.8[b]	9.1	41	33	18	D_9-克仑特罗
	276.9/258.9		41	31	8	
醋酸可的松 cortisone acetate	403.4/343.2[b]	11.2	51	27	6	
	403.4/163.2		36	39	4	
结晶紫 crystal violet	372.2/356.2[b]	11	56	65	16	D_6-结晶紫
	372.2/251.2		56	37	12	
D_3-沙丁胺醇 D_3-salbutnol	243.1/224.9	6.7	61	45	16	
D_5-氯丙嗪 D_5-chlorpromazine	325.1/91.8	10.9	41	31	14	
D_3-莱克多巴胺 D_3-ractopamine	308.2/290.2	8.7	51	31	8	
D_6-隐性结晶紫 D_6-leuco crystal violet	380.2/245	10.9	36	29	6	
D_5-孔雀石绿 D_6-malachite green	334.1/318	10.7	51	65	10	

表 C.1（续）

化合物[a]	离子对 Q1/Q3(m/z)	保留时间 min	去簇电压(DP)/V	碰撞气能量(CE)/eV	碰撞室出口电压(CXP)/V	内标物
D_9-克伦特罗 D_9-clentuterol	286/267.9	9.1	36	61	4	
D_3-洛硝哒唑 D_3-ronidazole	204/143	7.1	40	9	8	
D_6-结晶紫 D_6-crystal violet	378.3/362.2	11	188	40	20	
D_6-隐性孔雀石绿 D_6-leuco malachite green	380/239	10	110	48	11	
地西泮 diazepam	285.2/193[b]	11.7	36	29	6	
	285.2/154		51	65	10	
地美硝唑 dimetronidazole	142/96.0[b]	7.2	56	37	12	
	142/81.0		61	37	12	
表睾酮 epiandrosterone	289.4/108.9[b]	12.2	61	37	12	
	289.4/96.9		61	45	16	
非诺特罗 fenoterol	304.2/286.2[b]	7.5	36	29	6	
	304.2/107		51	65	10	
氟氢可的松 fludrocorisone	381.1/239[b]	7.5	36	61	4	
	381.1/181		36	29	6	
羟甲基甲硝咪唑 HMMNI	158/140.2[b]	7.5	36	61	4	
	158/55.0		36	29	6	
氟甲睾酮 fluoxymesterone	337.4/241[b]	11.6	61	45	16	
	337.4/131		41	31	14	
氢化可的松 hydrocortisone	363.2/121[b]	11	41	31	8	
	363.2/309.0		41	29	6	
异丙硝唑 ipronidazole	170.2/108.9[b]	10	31	29	14	
	170.2/123.0		51	33	10	
隐性结晶紫 leuco crystal violet	374.2/239.0[b]	11.1	41	31	14	D_6-隐性结晶紫
	374.2/358.1		41	33	18	
隐性孔雀石绿 leuco malachite green	331.2/315.3[b]	12.5	36	39	12	D_6-隐性孔雀石绿
	331.2/239.1		36	39	4	
去氢甲睾酮 methandienone	301.4/121.2[b]	11.7	38	42	12	
	301.4/149		38	36	4	

表 C.1（续）

化合物[a]	离子对 Q1/Q3(m/z)	保留时间 min	去簇电压 (DP)/ V	碰撞气能量 (CE)/ eV	碰撞室出口电压 (CXP)/ V	内标物
甲睾酮 methyltestosterone	303.2/97[b]	12	51	31	8	
	303.2/108.9		31	31	10	
甲硝唑 metronidazole	172/128[b]	6.7	36	39	4	
	172/82		36	39	12	
孔雀石绿 malachite green	329.1/313.3[b]	10.7	41	29	6	D_5-孔雀石绿
	329.1/208.3		36	61	4	
丙酸诺龙 nandrolone 17-propionate	331.4/257.4[b]	13.2	56	65	16	
	331.4/275.0		56	37	12	
诺龙 nandrolone	275/109[b]	11.6	36	39	12	
	275/257		56	65	16	
莱克多巴胺 ractopamine	302.1/164.1[b]	8.7	51	27	6	D_5-莱克多巴胺
	302.1/283.9		36	39	4	
洛硝哒唑 ronidazole	201/140[b]	7	36	39	12	D_3-洛硝哒唑
	201/55		56	65	16	
沙丁胺醇 salbutnol	240.1/222[b]	6.7	56	65	16	D_3-沙丁胺醇
	240.1/148		56	37	12	
特布他林 terbutaline	226.1/152.1[b]	6.6	36	39	4	
	226.1/170		36	39	12	
丙酸睾酮 testosterone propionate	345.4/97.1[b]	13.6	41	33	18	
	345.4/109.1		41	31	14	
睾酮 testosterone	289.3/96.9[b]	11.8	31	29	14	
	289.3/108.9		51	33	10	
妥布特罗 tobututerol	228.2/172[b]	9.6	61	45	16	
	228.2/153.8		41	31	14	
曲安西龙 triamcinolonel	395.4/225.1[b]	10.5	31	31	10	
	395.4/357.4		31	29	14	
曲安奈德 triamcinolone acetonide	435.2/338.9[b]	11.3	51	33	10	
	435.2/396.9		51	37	12	
ESI^- 模式						
己二烯雌酚 dienestrol	265.1/92.9[b]	9.6	−95	−35	−15	D_8-己二烯雌酚
	265.1/249		−95	−35	−15	

表 C.1（续）

化合物[a]	离子对 Q1/Q3(m/z)	保留时间 min	去簇电压 (DP)/ V	碰撞气能量 (CE)/ eV	碰撞室出口电压 (CXP)/ V	内标物
己烯雌酚 diethylstilbestrol	267/250.9[b]	9.5	−115	−39	−13	
	267/237		−115	−46	−13	
己烷雌酚 hexestrol	269/134[b]	9.6	−75	−22	−11	
	269/119		−75	−42	−11	
D8-己二烯雌酚 D8-dienestrol	275/259	9.4	−108	−36	−13	
D5-氯霉素 D5-chloramphenicol	326/157.1	6.8	−51	−24	−10	
玉米赤霉烯酮 zearalenone	317.1/175[b]	9.7	−101	−32	−5	
	317.1/131		−51	−40	−5	
α-玉米赤霉烯醇 α-zearalenol	319.1/301.1[b]	8.8	−111	−30	−5	
	319.1/275.2		−111	−29	−5	
β-玉米赤霉烯醇 β-zearalenol	319.1/301.1[b]	8.3	−111	−42	−5	
	319.1/275.2		−111	−29	−5	
玉米赤霉酮 zearalanone	319.1/301.1[b]	9.6	−111	−42	−5	
	319.1/275.2		−111	−29	−5	
氯霉素 chloramphenicol	321/152[b]	6.8	−65	−25	−7	D_5-氯霉素
	321/257		−101	−42	−5	
α-玉米赤霉醇 α-zeranol	321/227.2[b]	8.7	−101	−29	−5	
	321/303.4		−101	−42	−7	
β-玉米赤霉醇 β-zeranol	321/227.2[b]	8.2	−101	−29	−5	
	321/303.4		−101	−42	−7	

非商业性声明：表 C.1 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。

[a] 化合物按照英文名称首字母排序。

[b] 定量离子对。

附 录 D
（资料性附录）
典 型 谱 图

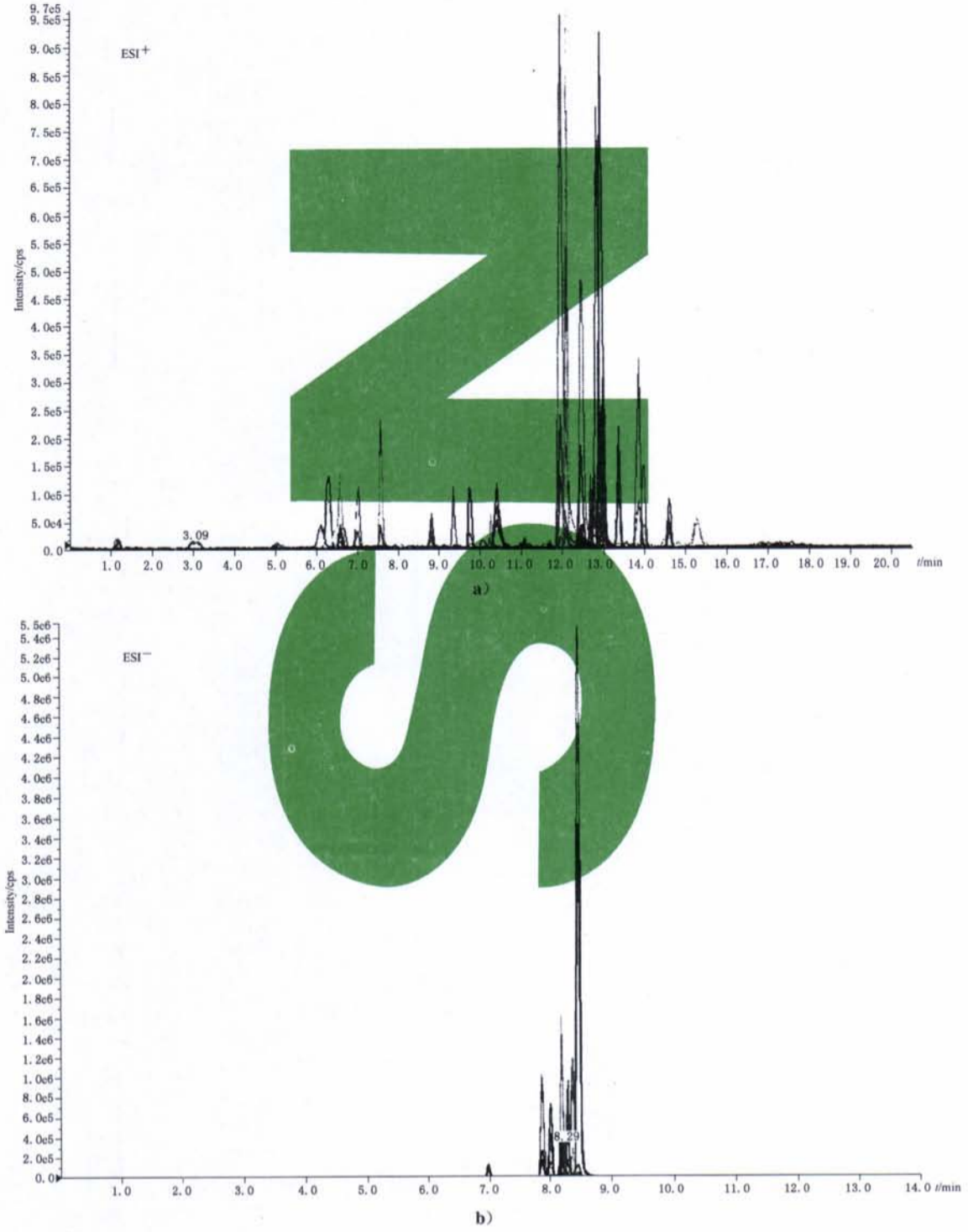


图 D.1 44 种药物标准物质的总离子流色谱图

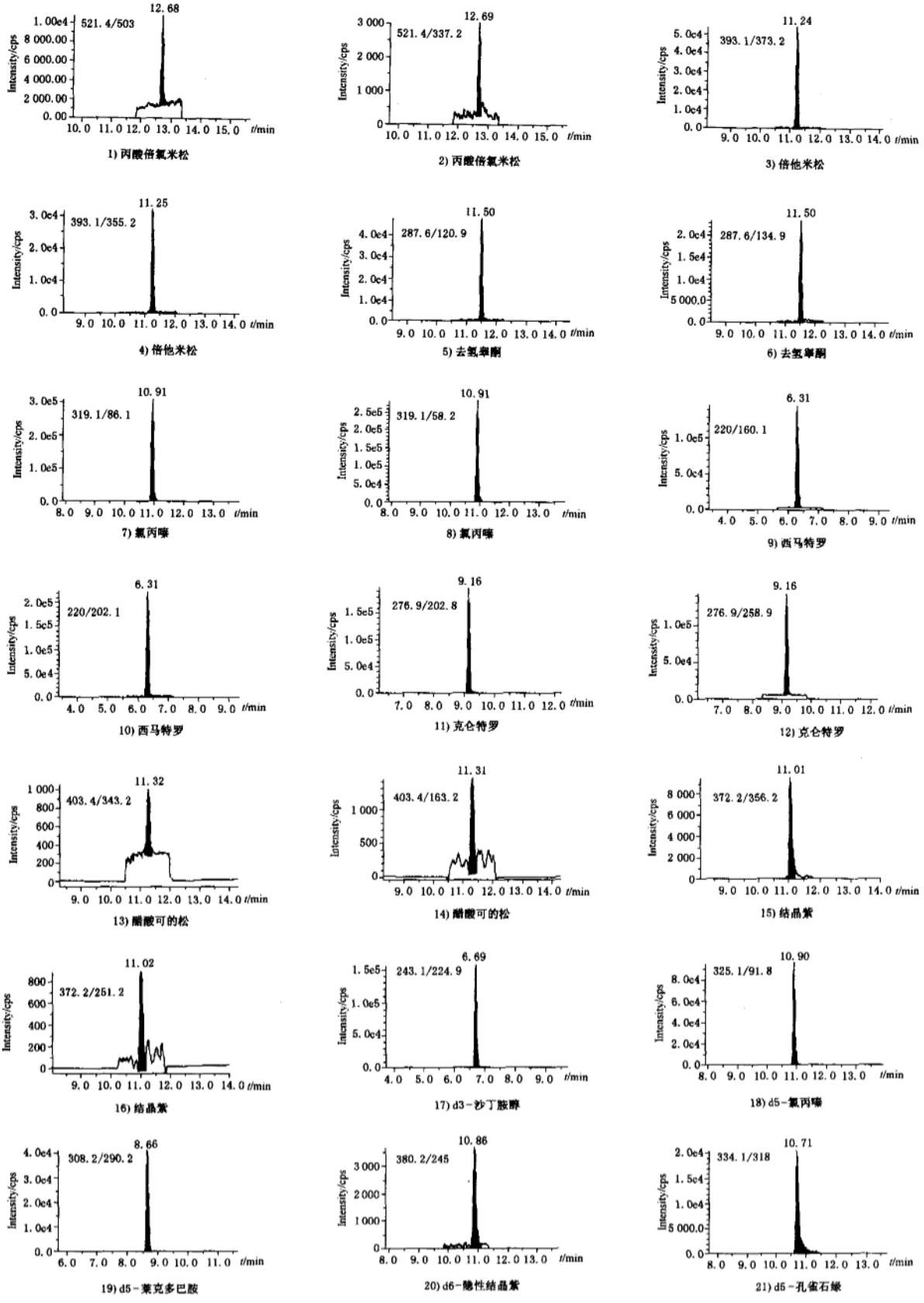
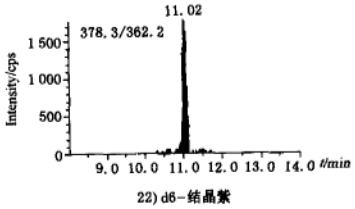
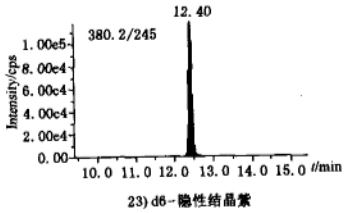


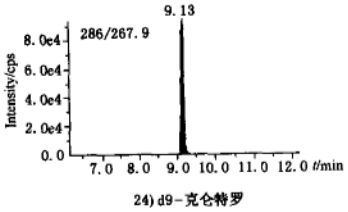
图 D.2　44 种药物及内标物的重构离子色谱图



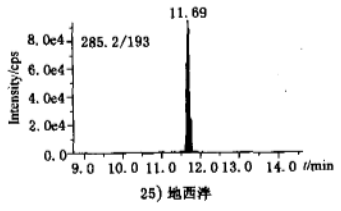
22) d6-结晶紫



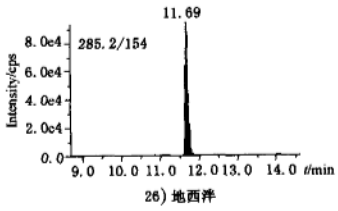
23) d6-隐性结晶紫



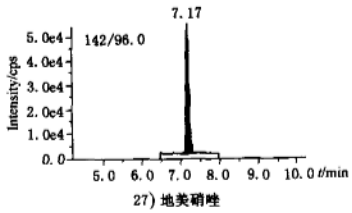
24) d9-克仑特罗



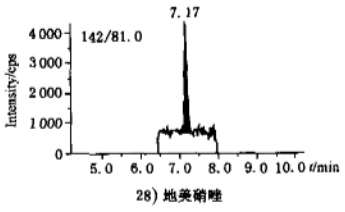
25) 地西泮



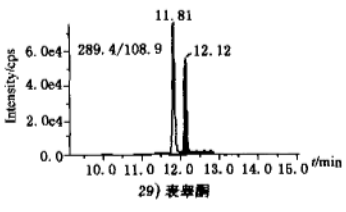
26) 地西泮



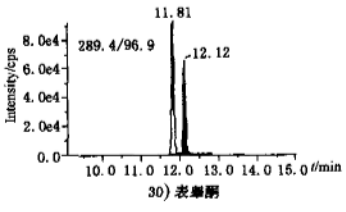
27) 地美硝唑



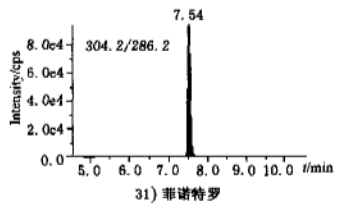
28) 地美硝唑



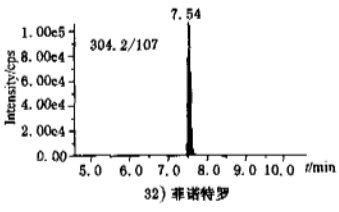
29) 表睾酮



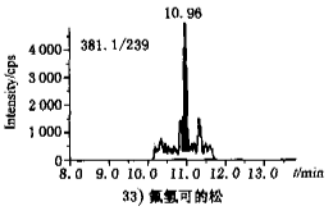
30) 表睾酮



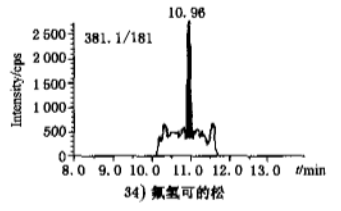
31) 非诺特罗



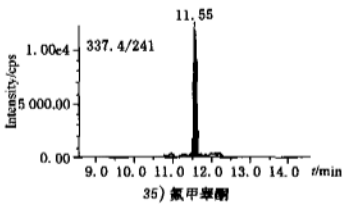
32) 非诺特罗



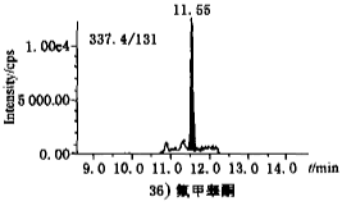
33) 氟氢可的松



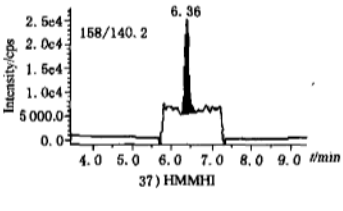
34) 氟氢可的松



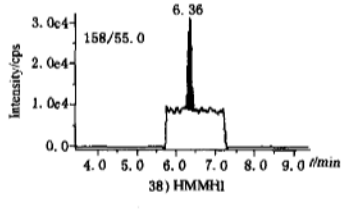
35) 氟甲睾酮



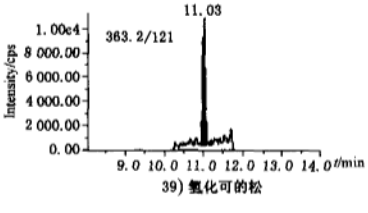
36) 氟甲睾酮



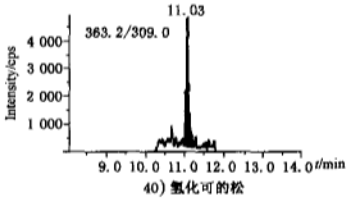
37) HMMHI



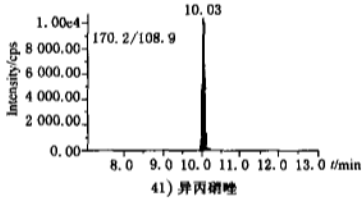
38) HMMHI



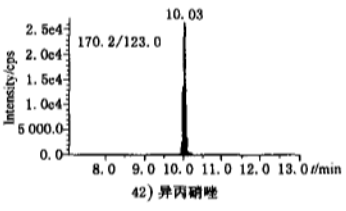
39) 氢化可的松



40) 氢化可的松



41) 异丙硝唑



42) 异丙硝唑

图 D.2（续）

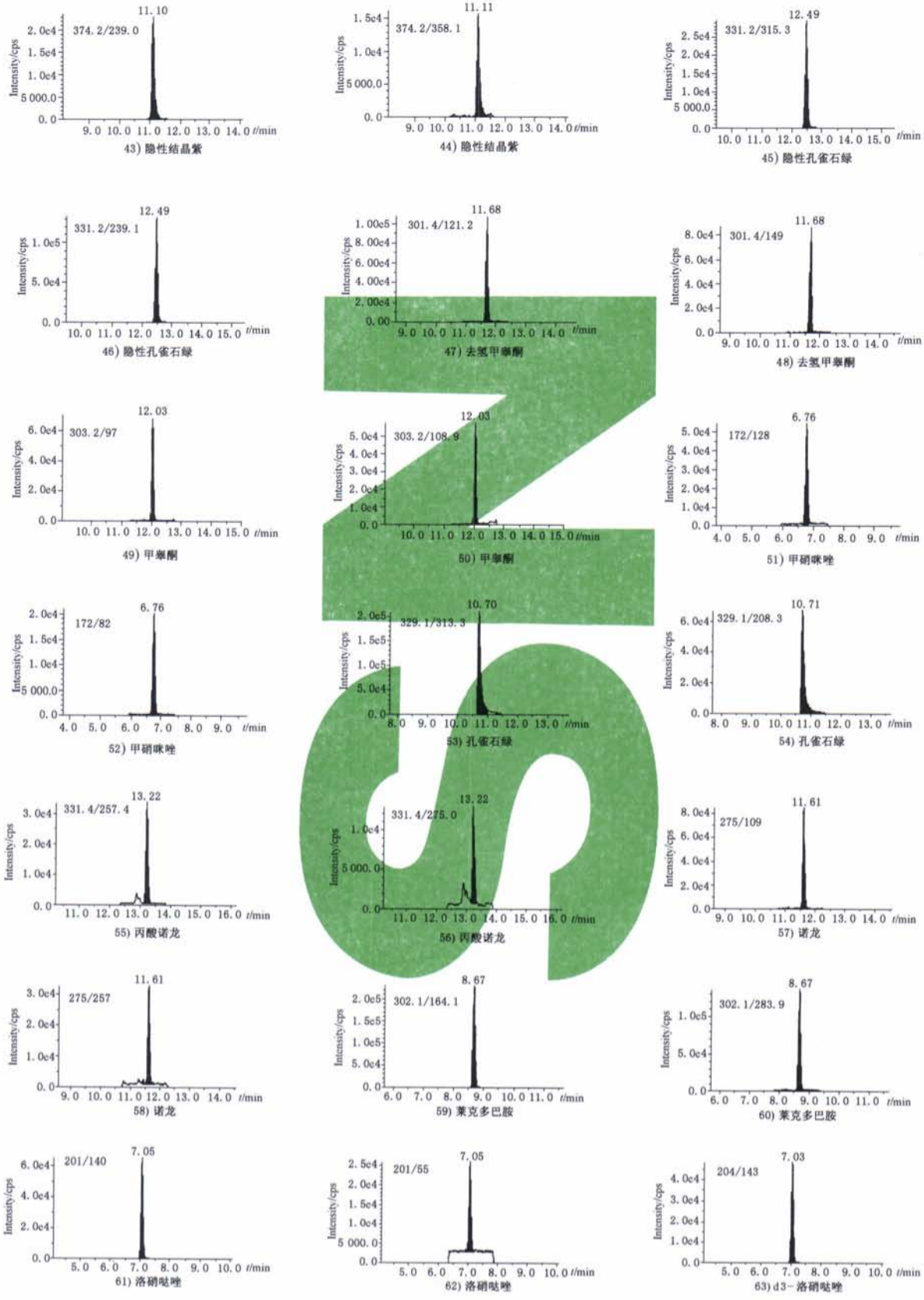

11.10
374.2/239.0
43) 隐性结晶紫
11.11
374.2/358.1
44) 隐性结晶紫
12.49
331.2/315.3
45) 隐性孔雀石绿
12.49
331.2/239.1
46) 隐性孔雀石绿
11.68
301.4/121.2
47) 去氢甲睾酮
11.68
301.4/149
48) 去氢甲睾酮
12.03
303.2/97
49) 甲睾酮
12.03
303.2/108.9
50) 甲睾酮
6.76
172/128
51) 甲硝咪唑
6.76
172/82
52) 甲硝咪唑
10.70
329.1/313.3
53) 孔雀石绿
10.71
329.1/208.3
54) 孔雀石绿
13.22
331.4/257.4
55) 丙酸诺龙
13.22
331.4/275.0
56) 丙酸诺龙
11.61
275/109
57) 诺龙
11.61
275/257
58) 诺龙
8.67
302.1/164.1
59) 莱克多巴胺
8.67
302.1/283.9
60) 莱克多巴胺
7.05
201/140
61) 洛硝哒唑
7.05
201/55
62) 洛硝哒唑
7.03
204/143
63) d3-洛硝哒唑

图 D.2（续）

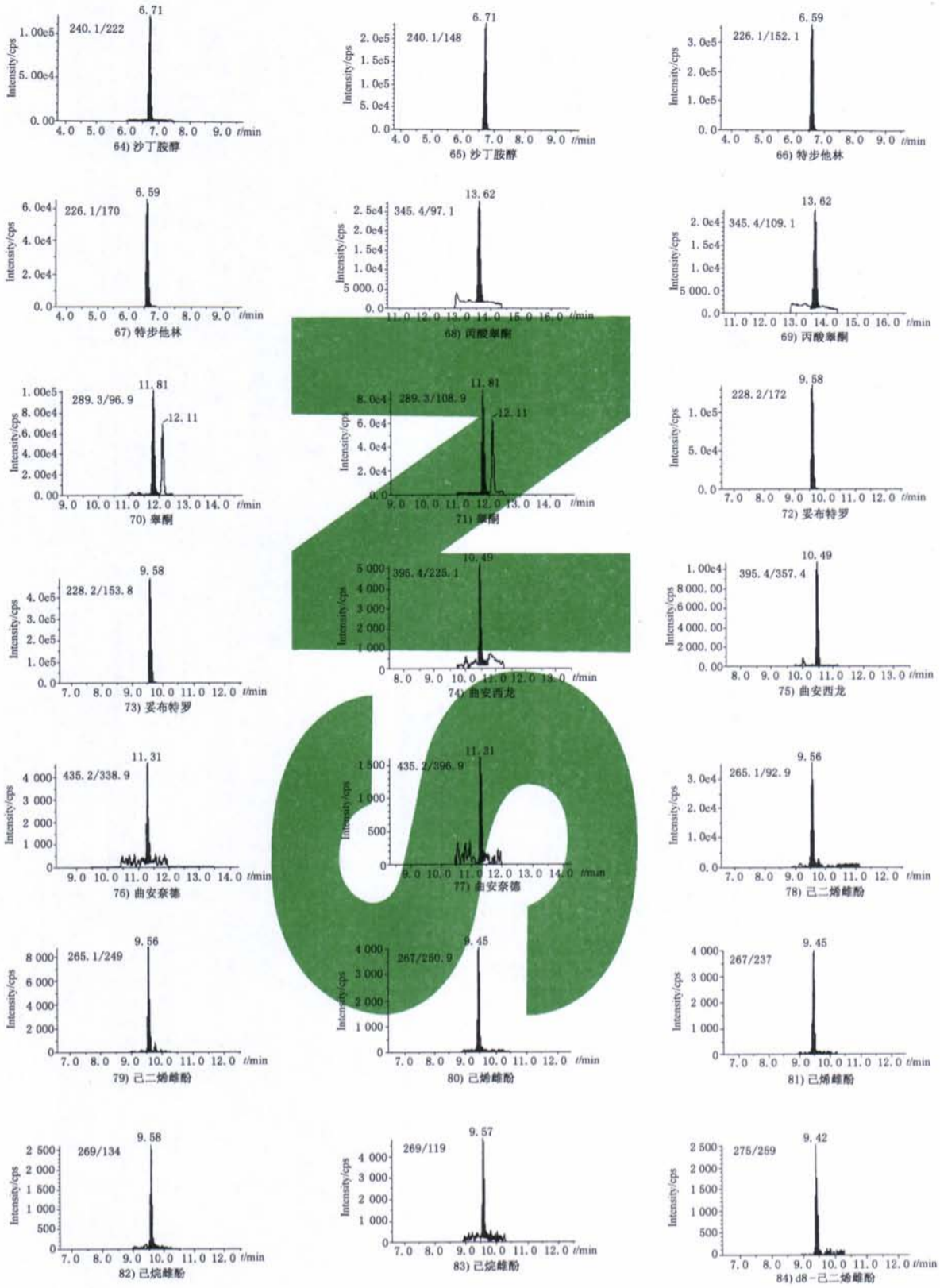

6.71
240.1/222
64) 沙丁胺醇
6.71
240.1/148
65) 沙丁胺醇
6.59
226.1/152.1
66) 特步他林
6.59
226.1/170
67) 特步他林
13.62
345.4/97.1
68) 丙酸睾酮
13.62
345.4/109.1
69) 丙酸睾酮
11.81
289.3/96.9
12.11
70) 睾酮
11.81
289.3/108.9
12.11
71) 睾酮
9.58
228.2/172
72) 妥布特罗
9.58
228.2/153.8
73) 妥布特罗
10.49
395.4/225.1
74) 曲安西龙
10.49
395.4/357.4
75) 曲安西龙
11.31
435.2/338.9
76) 曲安奈德
11.31
435.2/396.9
77) 曲安奈德
9.56
265.1/92.9
78) 己二烯雌酚
9.56
265.1/249
79) 己二烯雌酚
9.45
267/250.9
80) 己烯雌酚
9.45
267/237
81) 己烯雌酚
9.58
269/134
82) 己烷雌酚
9.57
269/119
83) 己烷雌酚
9.42
275/259
84) d8-己二烯雌酚
Intensity/cps
t/min

图 D.2（续）

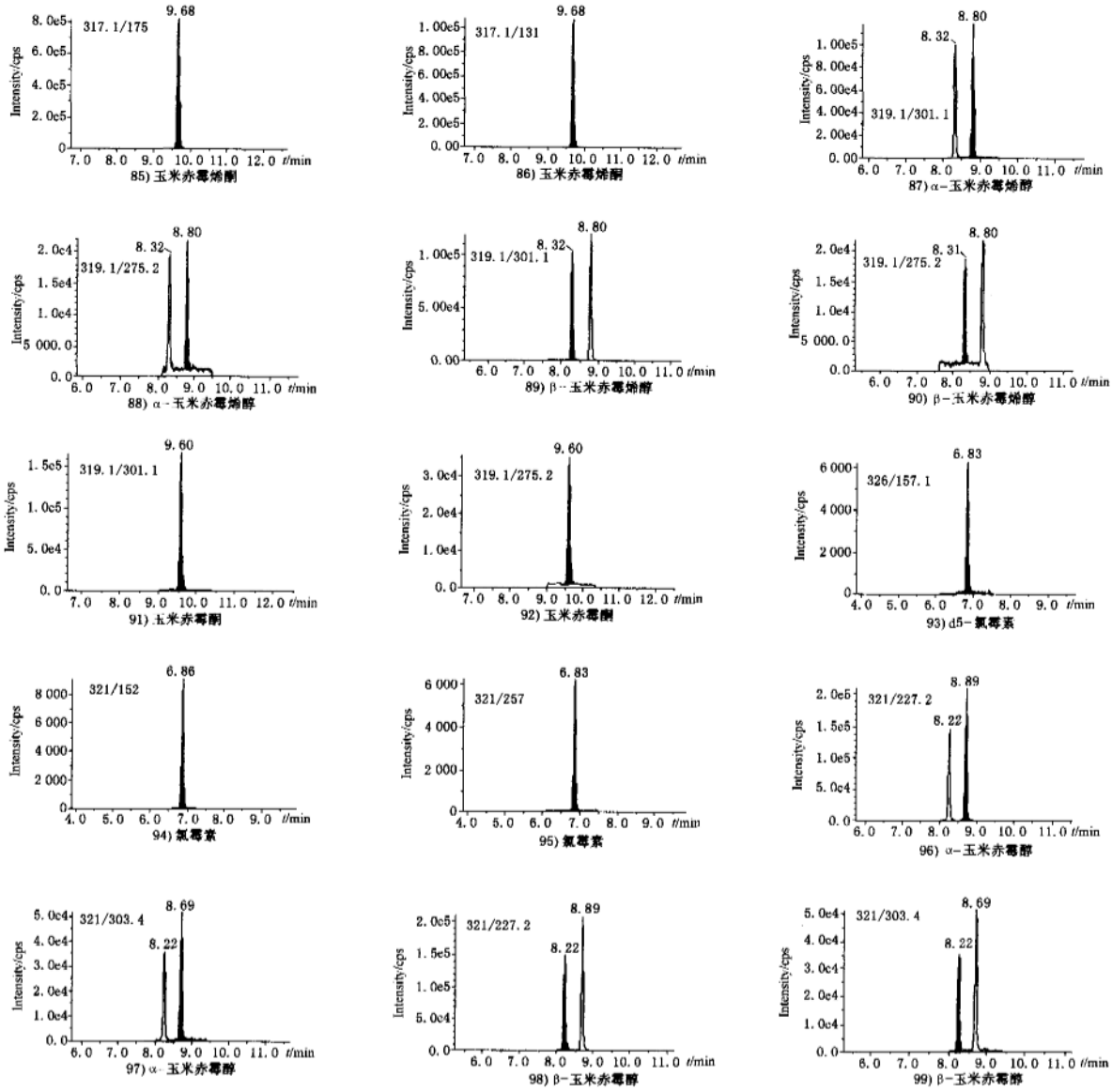

9.68
317.1/175
Intensity/cps
t/min
85) 玉米赤霉烯酮
9.68
317.1/131
86) 玉米赤霉烯酮
8.80
8.32
319.1/301.1
87) α-玉米赤霉烯醇
8.80
8.32
319.1/275.2
88) α-玉米赤霉烯醇
8.80
8.32
319.1/301.1
89) β-玉米赤霉烯醇
8.80
8.31
319.1/275.2
90) β-玉米赤霉烯醇
9.60
319.1/301.1
91) 玉米赤霉酮
9.60
319.1/275.2
92) 玉米赤霉酮
6.83
326/157.1
93) d5-氯霉素
6.86
321/152
94) 氯霉素
6.83
321/257
95) 氯霉素
8.89
8.22
321/227.2
96) α-玉米赤霉醇
8.69
8.22
321/303.4
97) α-玉米赤霉醇
8.89
8.22
321/227.2
98) β-玉米赤霉醇
8.69
8.22
321/303.4
99) β-玉米赤霉醇

图 D.2（续）

附 录 E
（资料性附录）
方法测定低限汇总表

表 E.1 方法的测定低限(基质:牛奶)

序号	化 合 物		测定低限 μg/kg	序号	化 合 物		测定低限 μg/kg
1	β-受体激动剂类	西玛特罗	0.5	17	二羟基苯甲酸内酯类	玉米赤霉烯酮	0.5
2		克仑特罗	0.5	18		α-玉米赤霉烯醇	1
3		菲诺特罗	1	19		β-玉米赤霉烯醇	1
4		莱克多巴胺	0.5	20		玉米赤霉酮	1
5		沙丁胺醇	0.5	21		α-玉米赤霉醇	1
6		特布他林	0.5	22		β-玉米赤霉醇	1
7		妥布特罗	0.5	23	硝基咪唑类	地美硝唑	0.5
8	雄性激素类	去氢睾酮	1	24		异丙硝唑	0.5
9		表睾酮	1	25		甲硝唑	0.5
10		去氢甲睾酮	1	26		洛硝哒唑	0.5
11		诺龙	1	27	雌性激素类	己二烯雌酚	1
12		睾酮	1	28		己烯雌酚	1
13	糖皮质激素类	丙酸倍氯米松	1	29		己烷雌酚	1
14		倍他米松	0.5	30	镇静剂类	氯丙嗪	0.5
15		曲安西龙	0.5	31		地西泮	0.5
16		曲安奈德	1	32	氯霉素	氯霉素	0.05

表 E.2 方法的测定低限(基质:猪肝)

序号	化 合 物		测定低限 μg/kg	序号	化 合 物		测定低限 μg/kg
1	β-受体激动剂类	西玛特罗	0.5	10	雄性激素类	诺龙	1
2		克仑特罗	0.5	11		睾酮	1
3		莱克多巴胺	0.5	12	糖皮质激素类	倍他米松	1
4		沙丁胺醇	0.5	13		氢化可的松	1
5		特布他林	0.5	14		曲安西龙	1
6		妥布特罗	0.5	15		曲安奈德	1
7	雄性激素类	去氢睾酮	1	16	二羟基苯甲酸内酯类	玉米赤霉烯酮	0.5
8		表睾酮	0.5	17		α-玉米赤霉烯醇	1
9		甲睾酮	1	18		β-玉米赤霉烯醇	1

表 E.2（续）

序号	化合物		测定低限 μg/kg	序号	化合物		测定低限 μg/kg
19	二羟基苯甲酸内酯类	玉米赤霉酮	0.5	26	雌性激素类	己二烯雌酚	1
20		α-玉米赤霉醇	1	27		己烯雌酚	1
21		β-玉米赤霉醇	1	28		己烷雌酚	1
22	硝基咪唑类	洛硝哒唑	0.5	29	镇静剂类	氯丙嗪	0.5
23		异丙硝唑	0.5	30		地西泮	0.5
24		甲硝唑	1	31	氯霉素	氯霉素	0.05
25		洛硝哒唑	0.5				

表 E.3 方法的测定低限（基质：鸡肉）

序号	化合物		测定低限 μg/kg	序号	化合物		测定低限 μg/kg
1	β-受体激动剂类	西玛特罗	0.5	17	二羟基苯甲酸内酯类	玉米赤霉烯酮	0.5
2		克仑特罗	0.5	18		α-玉米赤霉烯醇	1
3		菲诺特罗	1	19		β-玉米赤霉烯醇	1
4		莱克多巴胺	0.5	20		玉米赤霉酮	1
5		沙丁胺醇	0.5	21		α-玉米赤霉醇	1
6		特布他林	0.5	22		β-玉米赤霉醇	1
7		妥布特罗	0.5	23	硝基咪唑类	地美硝唑	0.5
8	雄性激素类	去氢睾酮	1	24		异丙硝唑	0.5
9		表睾酮	1	25		甲硝唑	0.5
10		去氢甲睾酮	1	26		洛硝哒唑	0.5
11		诺龙	1	27	雌性激素类	己二烯雌酚	1
12		睾酮	1	28		己烯雌酚	1
13	糖皮质激素类	丙酸倍氯米松	1	29		己烷雌酚	1
14		倍他米松	0.5	30	镇静剂类	氯丙嗪	0.5
15		曲安西龙	0.5	31		地西泮	0.5
16		曲安奈德	1	32	氯霉素	氯霉素	0.05

表 E.4 方法的测定低限（基质：猪肉）

序号	化合物		测定低限 μg/kg	序号	化合物		测定低限 μg/kg
1	β-受体激动剂类	西玛特罗	0.5	4	β-受体激动剂类	莱克多巴胺	0.5
2		克仑特罗	0.5	5		沙丁胺醇	0.5
3		菲诺特罗	1	6		特布他林	0.5

表 E.4（续）

序号	化合物		测定低限 μg/kg	序号	化合物		测定低限 μg/kg
7	β-受体激动剂类	妥布特罗	0.5	20	二羟基苯甲酸内酯类	玉米赤霉酮	1
8	雄性激素类	去氢睾酮	1	21		α-玉米赤霉醇	1
9		表睾酮	1	22		β-玉米赤霉醇	1
10		去氢甲睾酮	1	23	硝基咪唑类	地美硝唑	0.5
11		诺龙	1	24		异丙硝唑	0.5
12		睾酮	1	25		甲硝唑	0.5
13	糖皮质激素类	丙酸倍氯米松	1	26		洛硝哒唑	0.5
14		倍他米松	0.5	27	雌性激素类	己二烯雌酚	1
15		曲安西龙	0.5	28		己烯雌酚	1
16		曲安奈德	1	29		己烷雌酚	1
17	二羟基苯甲酸内酯类	玉米赤霉烯酮	0.5	30	镇静剂类	氯丙嗪	0.5
18		α-玉米赤霉烯醇	1	31		地西泮	0.5
19		β-玉米赤霉烯醇	1	32	氯霉素	氯霉素	0.05

表 E.5 方法的测定低限（基质：鱼）

序号	化合物		测定低限 μg/kg	序号	化合物		测定低限 μg/kg
1	β-受体激动剂类	西玛特罗	0.5	17	糖皮质激素类	丙酸倍氯米松	1.0
2		克仑特罗	0.5	18		倍他米松	0.5
3		菲诺特罗	0.5	19		醋酸可的松	1.0
4		莱克多巴胺	0.5	20		氟氢可的松	1.0
5		沙丁胺醇	0.5	21		氢化可的松	1.0
6		特布他林	0.5	22		曲安西龙	1.0
7		妥布特罗	0.5	23		曲安奈德	1.0
8	雄性激素类	去氢睾酮	0.5	24	二羟基苯甲酸内酯类	玉米赤霉烯酮	0.5
9		表睾酮	0.5	25		α-玉米赤霉烯醇	0.5
10		氟甲睾酮	1	26		β-玉米赤霉烯醇	0.5
11		去氢甲睾酮	0.5	27		玉米赤霉酮	0.5
12		甲睾酮	1	28		α-玉米赤霉醇	0.5
13		丙酸诺龙	0.5	29		β-玉米赤霉醇	1
14		诺龙	0.5	30	硝基咪唑类	地美硝唑	0.5
15		丙酸睾酮	1	31		异丙硝唑	0.5
16		睾酮	1	32		甲硝唑	0.5

表 E.5（续）

序号	化合物		测定低限 μg/kg	序号	化合物		测定低限 μg/kg
33	硝基咪唑类	洛硝哒唑	0.5	39	镇静剂类	地西泮	0.5
34		羟甲基甲硝咪唑	1.0	40	氯霉素	氯霉素	0.05
35	雌性激素类	己二烯雌酚	1	41	三苯甲烷类	孔雀石绿	0.5
36		己烯雌酚	1	42		隐性孔雀石绿	0.5
37		己烷雌酚	1	43		结晶紫	0.5
38	镇静剂类	氯丙嗪	0.5	44		隐性结晶紫	0.5

附 录 F
（资料性附录）
添加回收率汇总表

表 F.1 牛奶基质中多类禁用药物添加回收率范围（$n=6$）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
丙酸倍氯米松 beclomethasone diptopionate	1	70.3～84.1	异丙硝唑 ipronidazole	0.5	92～105.2
	2	90.5～104.5		1	88.9～104
	4	92.25～103.75		2	86.5～92.5
倍他米松 betanethasone	0.5	95.6～108.8	去氢甲睾酮 methandienone	1	83.4～102
	1	97.5～113		2	94～104.5
	2	93.5～116		4	89.25～108.75
去氢睾酮 boldenone	1	96～112	甲硝唑 metronidazole	0.5	72.4～114
	2	88～112		1	90.4～113
	4	97.75～114.5		2	78.5～115
氯丙嗪 chlorpromazine	0.5	81.6～100.4	诺龙 nandrolone	1	95.6～114
	1	83～111		2	93.5～112.5
	2	84～100		4	106.75～118.5
西玛特罗 cimaterol	0.5	75.6～118	莱克多巴胺 ractopamine	0.5	91.6～103.8
	1	78.6～114		1	87.4～103
	2	78.5～119		2	91.5～99.5
克仑特罗 clentuterol	0.5	98.2～110.6	洛硝哒唑 ronidazole	0.5	73.4～103.6
	1	92.6～99.9		1	92.1～117
	2	93～100.5		2	91.5～118.5
地西泮 diazepam	0.5	63.8～99.8	沙丁胺醇 salbutnol	0.5	80.8～112.8
	1	83.3～113		1	64.3～104
	2	72～110		2	65.5～103
地美硝唑 dimetronidazole	0.5	67.4～100.4	特布他林 terbutaline	0.5	75～107.2
	1	69.7～86.8		1	76.8～117
	2	76.5～102		2	98～111
表睾酮 epiandrosterone	1	89.2～111	睾酮 testosterone	1	84.7～98.3
	2	100～111.5		2	91～109
	4	103.5～108.5		4	99～109
非诺特罗 fenoterol	1	83.1～98	妥布特罗 tobututerol	0.5	70～118.2
	2	85.2～96.3		1	102～107
	4	81.6～99.2		2	99.5～104

表 F.1（续）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
曲安西龙 triamcinolonel	0.5	70～115.8	α-玉米赤霉烯醇 α-zearalenol	1	69.6～99.1
	1	97.3～117		2	85～110.5
	2	82～113.5		4	100～111.5
曲安奈德 triamcinolone acetonide	1	89.5～116	β-玉米赤霉烯醇 β-zearalenol	1	88.9～102
	2	97～118.5		2	100～108
	4	102～114.75		4	91～110.25
己二烯雌酚 dienestrol	1	102～118	玉米赤霉酮 zearalanone	1	72～92.1
	2	104～117.5		2	89～112.5
	4	90.3～114		4	92.25～117.25
己烯雌酚 diethylstilbestrol	1	76.1～108	氯霉素 chloramphenicol	0.05	77.6～106
	2	66.5～99.2		0.1	94.2～116
	4	76.8～106.25		0.2	95.5～124.5
己烷雌酚 hexestrol	1	63.9～91.2	α-玉米赤霉醇 α-zeranol	1	91.5～110
	2	71.5～112		2	103～124
	4	80～118.75		4	99.5～118.25
玉米赤霉烯酮 zearalenone	0.5	72.8～95.6	β-玉米赤霉醇 β-zeranol	1	89.5～106
	1	82.7～101		2	101～119
	2	91～118.5		4	96～114.25

表 F.2　猪肝基质中多类禁用药物添中回收率范围（$n=6$）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
倍他米松 betanethasone	1	102～120	克仑特罗 clentuterol	0.5	83～105
	2	99～112		1	66～108
	4	98.1～104		2	72.5～78.5
去氢睾酮 boldenone	1	89.8～111	地西泮 diazepam	0.5	91.6～115
	2	82～97.5		1	93.7～119
	4	82.3～95.5		2	86.5～110
氯丙嗪 chlorpromazine	0.5	96～116	地美硝唑 dimetronidazole	1	89.3～104
	1	93.7～109		2	87～95.5
	2	86.5～110		4	61.8～74.5
西码特罗 cimaterol	0.5	99.5～104	表睾酮 epiandrosterone	0.5	75～104
	1	105～118		1	82.1～107
	2	102～110		2	86～102

表 F.2（续）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
氟氢可的松 fiudro cortisone	1	76.8～93.1	曲安西龙 triamcinolonel	1	85.8～102
	2	76.4～99.5		2	74.5～98.5
	4	85.5～101		4	63.3～96.8
异丙硝唑 ipronidazole	0.5	94.2～102	曲安奈德 triamcinolone acetonide	1	76.5～93.3
	1	83.8～94.9		2	73.5～85
	2	89～98		4	66.5～85.8
甲睾酮 methyltestosterone	1	88.6～106	玉米赤霉烯酮 zearalenone	1	82.3～117
	2	92～104		2	75～109
	4	93.7～112		4	72～117
甲硝唑 metronidazole	1	87.3～91.9	α-玉米赤霉烯醇 α-zearalenol	1	101～118
	2	85.5～101		2	83.3～118
	4	78.3～94.5		4	84～119
诺龙 nandrolone	1	91～115	β-玉米赤霉烯醇 β-zearalenol	1	79.5～116
	2	99.5～105		2	70.5～119
	4	85～95.5		4	74.5～93.3
莱克多巴胺 ractopamine	0.5	109～119	玉米赤霉酮 zearalanone	0.5	99.6～115
	1	98.8～108		1	88.2～111
	2	94.5～98.5		2	85.1～93.7
洛硝哒唑 ronidazole	0.5	85.1～96.1	氯霉素 chloramphenicol	1	81～119
	1	82.3～99.2		2	81～96.5
	2	90.6～105		4	84.8～113
沙丁胺醇 salbutnol	0.5	76～106	α-玉米赤霉醇 α-zeranol	1	101～115
	1	70.1～88.2		2	83～108
	2	80.5～95.5		4	71～84
特布他林 terbutaline	0.5	96.8～115	β-玉米赤霉醇 β-zeranol	0.5	81.5～109
	1	96.1～118		1	71.2～107
	2	101～114		2	92～108
睾酮 testosterone	1	75.4～93.7	玉米赤霉烯酮 zearalenone	0.1	87.2～112
	2	83～99		0.2	86～104
	4	91.5～118		0.4	69～90
妥布特罗 tobututerol	0.5	101～117	α-玉米赤霉烯醇 α-zearalenol	1	70～103
	1	95～119		2	100～119
	2	108～115		4	102～118
			β-玉米赤霉烯醇 β-zearalenol	1	79.7～126
				2	69.3～105
				4	79.1～119

表 F.3 鸡肉基质中多类禁用药物添加回收率范围($n=6$)

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
丙酸倍氯米松 beclomethasone dipropionate	1	79.2～98.8	去氢甲睾酮 methandienone	1	88.1～104
	2	87.5～101		2	95.5～106
	4	89.8～98.5		4	96.1～98.1
倍他米松 betanethasone	0.5	92.4～107	甲硝唑 metronidazole	0.5	94.4～102
	1	99.1～113		1	92.8～97.5
	2	108～116		2	101～104
去氢睾酮 boldenone	1	79.9～110	诺龙 nandrolone	1	101～110
	2	94.1～118		2	101～119
	4	101～119		4	101～118
氯丙嗪 chlorpromazine	0.5	98.2～116	莱克多巴胺 ractopamine	0.5	97.6～115
	1	86.3～111		1	88.6～103
	2	102～116		2	86.5～116
西玛特罗 cimaterol	0.5	85.1～104	洛硝哒唑 ronidazole	0.5	86.1～102
	1	90.7～117		1	70.2～115
	2	97～113		2	111～115
克仑特罗 clentuterol	0.5	86.4～103	沙丁胺醇 salbutnol	0.5	86.4～111
	1	90.1～107		1	86.5～96.1
	2	90～106		2	86.5～92.5
地西泮 diazepam	0.5	87.8～99.2	特布他林 terbutaline	0.5	84.1～88.6
	1	81.5～92.7		1	90.9～96.6
	2	97.1～110		2	88.5～93.1
地美硝唑 dimetronidazole	0.5	91.6～101	睾酮 testosterone	1	89.7～98.2
	1	99.6～106		2	103～112
	2	109～112		4	99.5～109
表睾酮 epiandrosterone	1	100～108	妥布特罗 tobututerol	0.5	89.8～103
	2	107～117		1	90.2～101
	4	99.8～114		2	100～104
菲诺特罗 fenoterol	1	76.4～93.1	曲安西龙 triamcinolonel	0.5	86.3～102
	2	84.5～99.5		1	90.2～106
	4	86～99.5		2	102～117
异丙硝唑 ipronidazole	0.5	88.4～105	曲安奈德 triamcinolone acetonide	1	91.9～116
	1	94.2～102		2	95.1～106
	2	99.5～114		4	85.5～102

表 F.3（续）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
己二烯雌酚 dienestrol	1	85.4～112	β-玉米赤霉烯醇 β-zearalenol	1	99.1～116
	2	78.1～97.5		2	101～119
	4	67.5～107		4	93.2～113
己烯雌酚 diethylstilbestrol	1	104～119	玉米赤霉酮 zearalanone	1	66.8～83.9
	2	75.2～119		2	80.5～117
	4	89.2～114		4	67.8～100
己烷雌酚 hexestrol	1	65.1～94.5	氯霉素 chloramphenicol	0.05	70.8～88.1
	2	76.1～114		0.1	81.1～97.6
	4	70.1～113		0.2	86.1～99.1
玉米赤霉烯酮 zearalenone	0.5	90.2～104	α-玉米赤霉醇 α zeranol	1	71.7～99.1
	1	78.1～96.8		2	94.5～110
	2	96.1～120		4	80.2～116
α-玉米赤霉烯醇 α-zearalenol	1	75.1～87.1	β-玉米赤霉醇 β-zeranol	1	81.5～101
	2	80.5～117		2	93.1～114
	4	84.2～108		4	85.2～111

表 F.4 猪肉基质中多类禁用药物添加回收率范围（$n=6$）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
丙酸倍氯米松 beclomethasone diptopionate	1	89.2～112	克仑特罗 clentuterol	0.5	90～116.6
	2	98.5～117		1	95.1～106
	4	83.25～117.75		2	93.5～108
倍他米松 betanethasone	0.5	102～115	地西泮 diazepam	0.5	98.2～107.4
	1	102～117		1	87.9～114
	2	103～117.5		2	90～97
去氢睾酮 boldenone	1	101～117	地美硝唑 dimetronidazole	0.5	82.6～97.8
	2	80.5～109		1	64.7～72.9
	4	94.75～113.5		2	60～78.75
氯丙嗪 chlorpromazine	0.5	71.4～113.8	表睾酮 epiandrosterone	1	91.9～115
	1	73.6～89.5		2	91.75～108.25
	2	87.5～110		4	110.75～117.7
西玛特罗 cimaterol	0.5	104.4～109	非诺特罗 fenoterol	1	76.3～89.1
	1	80.9～92.6		2	82.1～96.4
	2	69.5～119		4	86.4～106

表 F.4（续）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
异丙硝唑 ipronidazole	0.5	91～109.4	曲安奈德 triamcinolone acetonide	1	74.3～84.5
	1	93.8～107		2	93.5～116
	2	85.5～103.75		4	96.75～113
去氢甲睾酮 methandienone	1	71.2～110	己二烯雌酚 dienestrol	1	89.4～104
	2	79.5～100.25		2	83.5～108.5
	4	101～113.75		4	100.2～115.75
甲硝唑 metronidazole	0.5	88.4～103.8	己烯雌酚 diethylstilbestrol	1	77.5～110
	1	79.7～105		2	89.5～108.5
	2	60.5～104.75		4	99.75～117.75
诺龙 nandrolone	1	80～112	己烷雌酚 hexestrol	1	65～97.5
	2	92.4～108		2	63.25～118.25
	4	101～116.75		4	74.75～102.25
莱克多巴胺 ractopamine	0.5	99.2～111.8	玉米赤霉烯酮 zearalenone	0.5	91.4～107
	1	90～93.9		1	95.7～117
	2	80～108		2	104～117.5
洛硝哒唑 ronidazole	0.5	85.6～112.8	α-玉米赤霉烯醇 α-zearalenol	1	88.5～119
	1	84.9～105		2	80.5～99.5
	2	84.5～104.25		4	67～79.75
沙丁胺醇 salbutnol	0.5	93.2～109.6	β-玉米赤霉烯醇 β-zearalenol	1	65.1～105
	1	95～105		2	69～106
	2	89.5～107		4	67.5～77
特布他林 terbutaline	0.5	103～118.2	玉米赤霉酮 zearalanone	1	83.1～95.2
	1	99.3～110		2	86.1～106
	2	99.5～117		4	92.3～105
睾酮 testosterone	1	92～118	氯霉素 chloramphenicol	0.05	67.2～88
	2	91.5～110		0.1	81.5～95.4
	4	100～114.75		0.2	93.5～110
妥布特罗 tobututerol	0.5	92.8～103.8	α-玉米赤霉醇 α-zeranol	1	87～117
	1	96.7～111		2	89～106
	2	84～115		4	88～104
曲安西龙 triamcinolonel	0.5	93.8～114.6	β-玉米赤霉醇 β-zeranol	1	71.8～79.1
	1	96.2～119		2	65～107.5
	2	91.5～114		4	58.2～78.5

表 F.5　鱼肉基质中多类禁用药物添加回收率范围(n=6)

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
丙酸倍氯米松 beclomethasone diptopionate	1	89.7～103	菲诺特罗 fenoterol	0.5	78.2～101
	2	81～100.5		1	86.1～103
	4	80.25～98.75		2	79.2～105
倍他米松 betanethasone	0.5	102.2～114.6	氟氢可的松 fludro cortisone	1	85.6～112
	1	95.1～101		2	73.5～99.5
	2	73～96.5		4	82.5～93.5
去氢睾酮 boldenone	0.5	93.8～108.2	氟甲睾酮 fluoxymerostero	1	82.9～113
	1	80～101		2	93～108.5
	2	78.5～100.5		4	78.5～94.75
氯丙嗪 chlorpromazine	0.5	101.4～109.6	羟甲基甲硝咪唑 HMMNI	1	93.7～101
	1	93.2～104		2	83.5～106
	2	87～97		4	80.75～90.75
西玛特罗 cimaterol	0.5	61～94.6	氢化可的松 hydrocortisone	1	70.9～110
	1	60.5～92.2		2	76.5～110.5
	2	76.5～90.5		4	86.25～103.5
克仑特罗 clentuterol	0.5	99.6～110	异丙硝唑 ipronidazole	0.5	106～117.8
	1	93.1～101		1	94.1～118
	2	94～99.5		2	86.5～105.5
醋酸可的松 corisone acetate	1	80.4～107	隐性结晶紫 leuco crystal violet	0.5	68.2～110.4
	2	84.5～100		1	82.7～114
	4	82.5～95.25		2	90.1～119
结晶紫 crystal violet	0.5	100～119.8	隐性孔雀石绿 leuco malachite green	0.5	102～119.8
	1	85.3～105		1	82.8～98
	2	82～108.5		2	77.5～97
地西泮 diazepam	0.5	84～108	去氢甲睾酮 methandienone	0.5	93.2～112.2
	1	83.5～92.1		1	81～92.7
	2	76.5～107		2	83.5～98.5
地美硝唑 dimetronidazole	0.5	102～118.6	甲睾酮 methyltestosterone	1	80.7～104
	1	95.5～109		2	67.5～99.5
	2	91.5～111		4	84～96.2
表睾酮 epiandrosterone	0.5	94.2～110	甲硝唑 metronidazole	0.5	70.6～106.6
	1	86～113		1	69.6～82.3
	2	77～103.5		2	69～95

表 F.5（续）

化合物	添加浓度 μg/kg	回收率范围 %	化合物	添加浓度 μg/kg	回收率范围 %
孔雀石绿 malachite green	0.5	84.4～103.2	曲安奈德 triamcinolone acetonide	1	81.2～107
	1	76.5～95.2		2	83～111.5
	2	64.5～99		4	74.25～85.75
丙酸诺龙 nandrolone 17-propionate	0.5	88.2～103	己二烯雌酚 dienestrol	1	79.7～105
	1	85.2～110		2	91～108
	2	83～102		4	74.5～108.25
诺龙 nandrolone	0.5	97.8～114	己烯雌酚 diethylstilbestrol	1	85.1～98.7
	1	90.6～102		2	63.5～108.5
	2	79～106		4	56～91
莱克多巴胺 ractopamine	0.5	95～107	己烷雌酚 hexestrol	1	71.8～95.5
	1	86.9～94.7		2	63.5～94
	2	87.5～106.5		4	67.5～99
洛硝哒唑 ronidazole	0.5	103～110	玉米赤霉烯酮 zearalenone	0.5	96.8～118.6
	1	94.8～106		1	75.3～107
	2	90.5～99.5		2	72～94
沙丁胺醇 salbutnol	0.5	84.2～117.2	α-玉米赤霉烯醇 α-zearalenol	0.5	83.4～107
	1	70.8～108		1	81.6～91.6
	2	89～108		2	79.5～95.5
特布他林 terbutaline	0.5	78.6～115	β-玉米赤霉烯醇 β-zearalenol	0.5	88.6～109.8
	1	68.2～91.3		1	81.6～101
	2	80.5～94		2	74.5～106
丙酸诺龙 nandrolone 17-proponate	1	85.2～115	玉米赤霉酮 zearalanone	0.5	70.3～99.2
	2	85.5～103		1	76.2～96.3
	4	91～114		2	83.1～99.3
睾酮 testosterone	1	88.7～106	氯霉素 chloramphenicol	0.05	85.6～114
	2	81～105.5		0.1	69.6～119
	4	80.5～90.75		0.2	68.5～109
妥布特罗 tobututerol	0.5	72.8～94	α-玉米赤霉醇 α-zeranol	0.5	101～111.4
	1	86.4～94.2		1	86.1～112
	2	86.5～108		2	88.5～100
曲安西龙 triamcinolonel	1	84.9～114	β-玉米赤霉醇 β-zeranol	1	92.4～116
	2	88～106		2	90.5～100
	4	85.75～106		4	89.75～100

Forward

This standard was drafted on the basis of the requirement of GB/T 1.1—2009.

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

The standard was drafted by Shenzhen and Shanghai Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China and Shenzhen University.

The main drafters of this standard are Yue Zhenfeng, Zhang Yi, Zhao Fengjuan, Hu Xiaoyuan Zhu Jian, Deng Xiaojun, Xiao Chengui, Chen Xiaoxia, Lan Fang, Ouyang Shan, Wen yanling, Lilisu.

Determination of multi-groups of banned drug residues in foodstuffs of animal origin for export—LC-MS/MS Method

1 Scope

This standard specifies the methods of β-agonist, androgens, glucocorticoids, estrogens, nitroimidazoles, resorcylic acid lactones, triphenylmethanes, sedatives and chloramphenicol residues in foodstuffs of animal origin for export—LC-MS/MS method. Thebanned drug introduction see annex A.

This srandard is adped to determination and screening of cimaterol, cimaterol, fenoterol, ractopamine, salbutamol, terbutaline, tulobuterol, boldenone, epiandrosterone, dehydro-17a-methyltestrosterone, nandrolone, testostrone, beclomethasone dipropionate, betamethasone, triamicinolone, triamcinolone acetonide, zearalenone, α-zearalenol, β-zearalenol, zearalanone, α-zeranol, β-zeranol, dimetronidazole, ipronidazole, metronidazole, ronidazole, dienestrol, diethylstilbestrol, hexestrol, chlorpromazine, diazapamand chloramphenicol in milk, chicken and pork samples.

This srandard is adped to determination and screening of cimaterol, cimaterol, ractopamine, salbutamol, terbutaline, tulobuterol, boldenone, epiandrosterone, methyltestosterone, nandrolone, testostrone, beclomethasone dipropionate, betamethasone, triamicinolone, triamcinolone acetonide, acetonide, zearalenone, α-zearalenol, β-zearalenol, zearalanone, α-zeranol, β-zeranol, dimetronidazole, ipronidazole, metronidazole, ronidazole, dienestrol, diethylstilbestrol, hexestrol, chlorpromazine, diazapamand chloramphenicol in liver sample.

This srandard is adped to determination and screening of cimaterol, cimaterol, fenoterol, ractopamine, salbutamol, terbutaline, tulobuterol, boldenone, epiandrosterone, fluoxymesterone, dehydro-17a-methyltestrosterone, methyltestosterone, nandrolone 17-propionate, nandrolone, testosterone propionate, testostrone, beclomethasone dipropionate, betamethasone, cortisone acetate, fiudrocortisone, hydrocortisone, triamicinolone, triamcinolone acetonide, zearalenone, α-zearalenol, β-zearalenol, zearalanone, α-zeranol, β-zeranol, dimetronidazole, ipronidazole, metronidazole, ronidazole, 1-methyl-5-nitro-1H-imidazole, dienestrol, diethylstilbestrol, hexestrol, chlorpromazine, diazapamand, chloramphenicol, malachite green, leuco malachite green, crystal violet and leuco crystal violet in fish sample.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this standard. For dated references, subsequent amendments to, or revisions of

any of these publications do not apply. However parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies.

GB/T 6682 Water for analytical laboratory use—specification and test methods

3 Sample preparation and storage

3.1 Animal liver, muscle and aquatic product

About 500 g representative edible samples should be taken from all samples, then grinded and blended by a tissue blender to produce homogenous samples, put in suitable clean containers. After being sealed and labeled, the samples should be stored at below −18 ℃.

3.2 Milk

About 500 mL representative samples should be taken from all samples, then mixed to produce homogenous samples, and put in suitable clean containers. After being sealed and labeled, the samples should be stored at below −18 ℃.

4 Principle

Aquatic product was extracted by using ammonia acetonitrile and acidified acetonitrile in turn. Other types samples were extracted with ammonia acetonitrile and acidified acetonitrile after enzymolysis in buffer condition. The extrates was cleaned up by a modified QuEChERS sorbents, and then was concentrated and reconstituted. The resultant elution was determined by LC-MS/MS, quantified by internal standard or external standard method.

5 Reagents and materials

Unless otherwise specified, all reagents should be of analytical grade; "Water" is the first grade water prescribed by GB/T 6682—1992.

5.1 Acetonitri le: HPLC Grade.

5.2 Methanol: HP LC Grade.

5.3 Glacial a cetic acid: HPLC Grade.

5.4 Ammonia:HPLC Grade.

5.5 Ammonium acetate:HPLC Grade.

5.6 Formic acid:HPLC Grade.

5.7 Glucuronidase/a rylsulfatase:Containing glucuronidase 134 600 U/mL,and arylsulfatase 5 200 U/mL.

5.8 Primary secondary amine sorbent (PSA):Diameter range of 40 μm～60 μm and average pore size of 100 Å.

5.9 Graphitized carbon black (GCB):diameter range of 40 μm～60 μm and average pore size of 60 Å.

5.10 Endcapped-C_{18} sorbent:diameter range of 40 μm～60 μm and average pore size of 60 Å.

5.11 Anh ydrous sodium sulfate:analytical Grade.

5.12 Anh ydrous magnesium sulfate:analytical Grade.

5.13 Acetate buffer:accurately weigh 7.7 g ammonium acetate (5.5) dissolved in 480 mL water, adjust pH value to 5.2 by glacial acetic acid(5.3),diluted with water to 500 mL,and mix to homogeneity.

5.14 1% Ammonia/acetonitrile solution:take 40 mL 25% ammonia (5.4) and 960 mL acetonitrile (5.1),and mix to homogeneity.

5.15 1% acetic acid/acetonitrile solution:take 10 mL acetic acid (5.3) and 990 mL acetonitrile (5.1) and mix to homogeneity.

5.16 20% acetonitrile/water solution:take 200 mL acetonitrile (5.1) and 800 mL water,and then mix to homogeneity.

5.17 0.1% formic acid solution:dilute 1 mL formic acid to 1 000 mL by water,and mix to homogeneity.

5.18 0.1% formic acid/methanol:dilute 1 mL formic acid to 1 000 mL by methanol (5.2),and mix to homogeneity.

5.19 QuEChERS sorbents 1 (applied to animal liver and musule sample):accurately weigh 100 mg of PSA (5.8),20 mg of GCB (5.9),50 mg of C_{18} (5.10) and 400 mg of anhydrous magnesium sulfate (5.12) in 25 mL centrifuge tube,and place in 25 mL centrifuge tube,screw the cap tightly for further use.

5.20 QuEChERS sorbents 2 (applied to milk and aquatic products): accurately weigh 100 mg of PSA, 40 mg of C_{18} and 600 mg of anhydrous magnesium sulfate, and place in 25 mL centrifuge tube, screw the cap tightly for further use.

5.21 Standard chemicals: β-agonists, androgens, glucocorticoids, estrogens, nitroimidazoles, Resorcylic acid lactones, chloramphenicol, Sedatives, malachite green, crystal violet and their metabolites were at 99% purityor above.

5.22 Intemal standard chemicals: D_3-salbutnol, d_5-chlorpromazine, d_5-ractopamine, d_6-1euco crystal violet, d_6-malachite green, d_9-clentuterol, d_3-ronidazole, d_8-crystal violet, D_6-leuco malachite green, D_8-dienestrol, D_5-chloramphenicol, D_8-dienestrol and D_5-chloramphenicol were at 95% purity or above.

5.23 Standard stock solution: accurately weigh considerable amount of standard chemical compounds of (5.21) dissolved in methanol and dilute to 10 mL, then mix to homogeneity. The concentration of the solution is 100.0 mg/L. The solution can be preserved in dark and at the temperature below −30 ℃ for more than 12 months.

5.24 Blank samples extracts: blank samples extract is obtained by prepared sample following with 7.1 and 7.2.

5.25 Mixed standard solution: accurately measure quantity sufficient standard stock solution (5.23) dilute with methanol to make the concentration of 1.0 mg/L and 0.1 mg/L. The solution can be preserved in dark and at the temperature below 4℃ for more than 6 months.

5.26 Mixed standard working solution: according to practice, mixed standard working solution is diluted with blank sample extract (5.24).

5.27 Internal standard stock solution: accurately weigh considerable amount of standard chemical compounds of (5.22) dissolved in methanol and dilute to 10 mL, then mix to homogeneity. The concentration of the solution is 100.0 mg/L. The solution can be preserved in dark and at the temperature below −30 ℃ for more than 12 months.

5.28 Mixed internal standard solution: accurately measure quantity sufficient standard stock solution (5.26) dilute with methanol to make the concentration of 1.0 mg/L and 0.1 mg/L. The solution can be preserved in dark and at the temperature below 4 ℃ for more than 6 months.

5.29 Mixed internal standard working solution: according to practice, mixed standard working solution is made by blank matrix just before use.

5.30 Millipore filiter: 0.22 μm.

6 Apparatus and equipment

6.1 High performance liquid chromatography-tandem quadrupole mass spectrometry or equivalent: equipped with electrospray ion source.

6.2 Analytical balance, sensitivity: 0.1 mg, 0.01 g.

6.3 Rotary evaporator.

6.4 Votex shaker.

6.5 High speed refrigerated centrifuge: 10 000 r/min.

6.6 Pipette: 10 μL～100 μL, 100 μL～1 000 μL.

6.7 pH meter.

6.8 Polypropylene centrifuge tube with screw-cap: 50 mL.

6.9 Tissue triturator.

6.10 Thermostatic waterbath.

6.11 Mechanical flat shaker.

7 Analytical procedure

7.1 Extraction procedure

7.1.1 Milk and animal tissues (liver, muscle)

Accurately 2 g sample weigh and transferred into a 50 mL polypropylene centrifuge tube with screw-cap, and spiked with 20 μL internal standard solution(5.28), and then were blended by a high-speed blender. 8 mL ammonium acetate buffer (5.13) was added, and samples were homogenized by vigorously shaking and vortex for 1 min. 30.0 μL glucuronidase/arylsulfatase (5.9) was added and incubated in thermostatic water-bath shaker at 37 ℃ for 12h. After cooling to room temperature, 5.0 g of anhydrous sodium sulfate (5.11) and 15.0 mL 1% ammonia/acetonitrile solution were added, and then homogenized for 30 sec at high speed, the mixture was centrifuged at 4 ℃ for 5 min at 9 500 r/min. Transfer the supernatant to another clean 50 mL centrifuge tube. 15 mL of 1% acetic acid/ace-

tonitrile solution(5. 15) was added into the remains, and vortex mixed for 1 min. The mixture was placed in mechanical flat shaker for 10 min and then under 4 ℃, centrifuged for 5 min at 9 500 r/min. The organic layer of twice extraction procedure was combined for the further purified.

7. 1. 2 Aquatic product (fish)

Accurately 2. 0 g sample weigh and transferred into a 50 mL polypropylene centrifuge tube with screw-cap, and spiked with internal standard and standard solution (5. 28), and then were blended by a high-speed blender. 8 mL ammonium acetate buffer (pH 5. 2) was added, and the sample were homogenized by vigorously shaking and vortex for 1 min, and then was placed at room temperature for 30 min. 5. 0 g of anhydrous sodium sulfate (5. 11) and 15. 0 mL 1% ammonia/acetonitrile solution were added, and then homogenized for 30 sec at high speed, the mixture was centrifuged at 4 ℃ for 5 min at 9 500 r/min. Transfer the supematant to another clean 50 mL centrifuge tube. 15 mL of 1% acetic acid/acetonitrile solution(5. 15) was added into the remains, and vortex mixed for 1 min. The mixture was placed in mechanical flat shaker for 10 min and then under 4 ℃, centrifuged for 5 min at 9 500 r/min. The organic layer of twice extraction procedure was combined for the further purified.

7. 2 Purification

The QuEChERS sorbets 1 was added into the milk and animal tissues extract, and QuEChERS sorbets 2 was placed into the aquatic product extract. The tube were tightly capped and shanken for 1 min, and was fiercely mixed by a vortex blender, were centrifuged at 9 500 rpm for 5 min at 4 ℃. The supernatant solution was taken into a 50 mL evaporated flask, and evaporated to approximate dryness by a vacuum parallel evaporator under 150 mbar at 42 ℃. The residue was reconstituted with 1. 0 mL of 20% acetonitrile/water solution (5. 16) by vortexing and ultrasonic, and the dilution was also filtered with a 0. 22 μm filter (5. 30) for further analysis.

7. 3 Determination

7. 3. 1 LC Conditions

7. 3. 1. 1 Column: C_{18} chromatography column, 3 μm particles diameter, 150 mm × 2. 1 mm(i. d).

7. 3. 1. 2 Mobile phase: A1: 0. 1% formic acid solution; B1: methanol; A2: acetonitrile, B2: water.

7. 3. 1. 3 Flow rate: 250 μL/min.

7. 3. 1. 4 Column temperature: 35 ℃.

7. 3. 1. 5 Injection volume: 10 μL.

7.3.1.6 gradient elution procedure list in table 1.

Table 1—Gradient elution procedure for positive and negative mode.

Positive(ESI^+)			Negative(ESI^-)		
Time min	A1 %	B1 %	Time min	A2 %	B2 %
0.00	95.0	10.0	0.00	80.0	20.0
4.00	45.0	55.0	8.00	2.0	98.0
5.00	5.0	95.0	9.00	2.0	98.0
8.00	5.0	95.0	10.00	80.0	20.0
13.00	95.0	5.0	18.00	80.0	20.0
22.00	95.0	5.0			

7.3.2 MS Conditions

7.3.2.1 Ionization mode:ESI; positive/negative acquiration mode.

7.3.2.2 Determination mode:MRM (retention time scheduled);

7.3.2.3 Resolution:unit resolution(see table B.1);

7.3.2.4 Other reference mass conditions are listed table C.1

7.3.3 HPLC-MS/MS determination

According to the approximate concentration of banned drug residues in the test sample solution, the standard working solution is selected with similar response to that of sample solution. The response of banned drug residues in the standard working solution and sample solution should be in the linear range of the instrumental response. The standard working solution should be injected randomly in between the injections of sample solution of equal volume. Schedule multi-reaction monitor (MRM) chromatogram and retention time of 44 standard compounds solution can be found Figure D.1

If the concentration exceeds the range of calibration curve, it is necessarily to dilute the analyte to appropriate concentration by methanol/water (1/9, v/v). Under optimal conditions, the chromatogram of each compound is given in figure D.2, and the retention time can reference table C.1(It is suggested that the positive results detected by this method need another method to confirm and quantify the substance).

7.4 Blank experiments

Except for spiked sample, the sample is pretreated according to the above procedure.

8 Calculation and result presentation

8.1 Qualitation criteria

8.1.1 Retention time

The variation range of the retention time for the peak of analyte in unknown sample and in the standard working solution can not be out of range of ±2.5% of retention time.

8.1.2 Qualitation ion, quantitation ion and ion ration between daughter ions.

The qualification ions for every compound must be found, and at least include one precursor ion and two daughter ions. For the same analysis batch and the same compound, the variation range of the ion ratio between the two daughter ions for the unknown sample and the standard working solution at the similar concentration can not be out of range of table 2.

Table 2—Maximum permitted tolerances of relative ion intensities for qualitation.

Relative ion intensity/%	>50	>20~50	>10~20	≤10
Permitted tolerances/%	±20	±25	±30	±50

8.2 Calculation and result presentation

The concentration of 44 target molecules were quantified by calibration curve method with following formula (1).

$$X = \frac{c \times V}{m} \times \frac{1\,000}{1\,000} \qquad \cdots\cdots(1)$$

Where

X —the residue content of the banned drug in the test sample, μg/kg;

c —concentration of the residues in calibration curve, μg/L;

V —the final volume of the test sample, mL.

m —weight of the sample, g.

9 Limit of determination and recovery

9.1 Limit of determination

The limit determination of this method in milk, liver, chicken, pork and fish were list in table E. 1～table E. 5.

9.2 Recovery

Recovery ranges of each compound in different matrix is listed C table F. 1～table F. 5.

Annex A
(informative annex)
Banned drug in introduction

Table A. 1—Banned drug introduction

Compound	CASNo	Structural formula	Molecular weight
β-agonists(7)			
clenbuterol	37148-27-9	$C_{12}H_{18}C_{12}N_2O$	277. 19
salbutamol	18559-94-9	$C_{13}H_{21}NO_3$	239. 31
ractopamine	97825-25-7	$C_{18}H_{23}NO_3$	301. 38
cimaterol	54239-37-1	$C_{12}H_{17}N_3O$	219. 28
terbutaline	23031-25-6	$C_{12}H_{19}NO_3$	225. 29
tulobuterol	41570-61-0	$C_{12}H_{18}ClNO$	227. 73
fenoterol	13392-18-2	$C_{17}H_{21}NO_4$	303. 35
Androgens(10)			
boldenone	846-48-0	$C_{19}H_{26}O_2$	286. 41
testosterone propionate	57-85-2	$C_{22}H_{32}O_3$	344. 49
dehydro-17a-methyltestrosterone	72-63-9	$C_{20}H_{28}O_2$	300. 44
methyltestosterone	58-18-4	$C_{20}H_{30}O_2$	302. 45
testostrone	58-22-0	$C_{19}H_{28}O_2$	288. 43
nandrolone 17-propionate	7207-92-3	$C_{21}H_{30}O_3$	330. 46
epiandrosterone	481-30-1	$C_{19}H_{28}O_2$	288. 42
fluoxymesterone	76-43-7	$C_{20}H_{29}FO$	336. 44
nandrolone	434-22-0	$C_{18}H_{26}O_2$	274. 40
nandrolone phenylpropionate	62-90-8	$C_{27}H_{34}O_3$	406. 56
Glucocorticoids(6)			
betamethasone	378-44-9	$C_{22}H_{29}FO_5$	392. 45
cortisone acetate	50-04-4	$C_{23}H_{30}O_6$	402. 49
beclomethasone dipropionate	4419-39-0	$C_{22}H_{29}ClO_5$	408. 92
hydrocortisone	50-23-7	$C_{21}H_{29}FO_5$	362. 47
triamicinolone	124-94-7	$C_{21}H_{30}O_5$	394. 44
triamcinolone acetonide	76-25-5	$C_{24}H_{27}FO_6$	434. 5
Estrogens(3)			
diethylstilbestrol	56-53-1	$C_{18}H_{20}O_2$	268. 35
hexestrol	84-16-2	$C_{18}H_{22}O_2$	270. 37
dienestrol	84-17-3	$C_{18}H_{18}O_2$	266. 33

Table A.1 (continued)

Compound	CASNo	Structural formula	Molecular weight
Nitroimidazoles(5)			
1-methyl-5-nitro-1*H*-imidazole (HMMNI)	936-05-0	$C_5H_7N_3O_3$	157.13
dimetronidazole	551-92-8	$C_5H_7N_3O_2$	157.13
ronidazole	7681-76-7	$C_6H_8N_4O_4$	200.15
metronidazole	443-48-1	$C_6H_9N_3O_3$	171.15
ipronidazole	14885-29-1	$C_7H_{11}N_3O_2$	169.18
Resorcylic acid lactones(6)			
α-zeranol	26538-44-3	$C_{18}H_{26}O_5$	322.4
β-zeranol	26538-44-3	$C_{18}H_{26}O_5$	322.4
α-zearalenol	36455-72-8	$C_{18}H_{24}O_5$	320.38
β-zearalenol	71030-11-0	$C_{18}H_{24}O_5$	320.38
zearalanone	5975-78-0	$C_{18}H_{24}O_5$	320.38
zearalenone	17924-92-4	$C_{18}H_{22}O_5$	318.36
Triphenylmethanes(4)			
malachite green	510-13-4	$C_{23}H_{26}N_2O$	346.46
leuco malachite green	129-73-7	$C_{23}H_{26}N_2$	330.47
crystal violet	548-62-9	$C_{25}H_{30}N_3Cl$	407.98
leuco crystal violet	603-48-5	$C_{25}H_{31}N_3$	373.53
Sedatives(2)			
chlorpromazine	50-53-3	$C_{17}H_{19}ClN_2S$	318.86
diazapam	439-14-5	$C_{16}H_{13}ClN_2O$	284.74
Chloramphenicol(1)			
chloramphenicol	439-14-5	$C_{11}H_{12}C_{12}N_2O_5$	323.13

Annex B
(informative annex)
Reference mass spectrometry conditions for API 5 000
tandem mass spectrometry

Table B. 1—Reference mass spectrometry conditions

Reference mass spectrometry conditions	Positive mode	Negative
Ion spray voltage	4 500 V	−4 500
Curtain gas pressure	1.7 bar	1.7 bar
Nebulizer gas pressure	3.4 bar	3.4 bar
Auxiliary gas pressure	4.4 bar	4.1 bar
Temperature	450 ℃	500 ℃

Annex C
(informative annex)
Main MS parameters of the banned drug

Table C. 1—Main MS parameters of the banned drug

Compound[a]	Ion pairs Q1/Q3(m/z)	Retention time min	Declustering potential (DP)/ V	Collision energy (CE)/ V	Collision cell exit potential (CXP)/ V	IS Standard
beclomethasone dipropionate	521. 4/503[b]	12. 7	51	37	12	
	521. 4/337. 2		51	71	4	
betamethasone	393. 1/373. 2[b]	11. 3	41	33	18	
	393. 1/355. 2		41	31	8	
boldenone	287. 6/120. 9[b]	11. 5	31	29	14	
	287. 6/134. 9		51	33	10	
chlorpromazine	319. 1/86. 1[b]	10. 9	56	65	16	D5-chlorpromazine
	319. 1/58. 2		56	37	12	
cimaterol	220/160. 1[b]	6. 3	41	31	8	
	220/202. 1		41	29	6	
clenbuterol	276. 9/202. 8[b]	9. 1	41	33	18	D9-clenbuterol
	276. 9/258. 9		41	31	8	
cortisone acetate	403. 4/343. 2[b]	11. 2	51	27	6	
	403. 4/163. 2		36	39	4	
crystal violet	372. 2/356. 2[b]	11	56	65	16	D6-crystal violet
	372. 2/251. 2		56	37	12	
D3-salbutamol	243. 1/224. 9	6. 7	61	45	16	
D5-chlorpromazine	325. 1/91. 8	10. 9	41	31	14	
D5-ractopamine	308. 2/290. 2	8. 7	51	31	8	
D6-leuco crystal violet	380. 2/245	10. 9	36	29	6	
D5-malachite green	334. 1/318	10. 7	51	65	10	
D9-clenbuterol	286/267. 9	9. 1	36	61	4	
D3-ronidazole	204/143	7. 1	40	9	8	
D6-crystal violet	378. 3/362. 2	11	188	40	20	
D6-leuco malachite green	380/239	10	110	48	11	
diazapam	285. 2/193[b]	11. 7	36	29	6	
	285. 2/154		51	65	10	

Table C. 1 (continued)

Compound[a]	Ion pairs Q1/Q3(*m/z*)	Retention time min	Declustering potential (DP)/ V	Collision energy (CE)/ V	Collision cell exit potential (CXP)/ V	IS Standard
dimetronidazole	142/96. 0[b]	7. 2	56	37	12	
	142/81. 0		61	37	12	
epiandrosterone	289. 4/108. 9[b]	12. 2	61	37	12	
	289. 4/96. 9		61	45	16	
fenoterol	304. 2/286. 2[b]	7. 5	36	29	6	
	304. 2/107		51	65	10	
fludrocorisone	381. 1/239[b]	7. 5	36	61	4	
	381. 1/181		36	29	6	
1-(2-hydroxyethyl)-2-hydroxymethyl-5-nitroimidazole(HMMNI)	158/140. 2[b]	7. 5	36	61	4	
	1 581/55. 0		36	29	6	
fluoxymesterone	337. 4/241[b]	11. 6	61	45	16	
	337. 4/131		41	31	14	
hydrocortisone	363. 2/121[b]	11	41	31	8	
	363. 2/309. 0		41	29	6	
ipronidazole	170. 2/108. 9[b]	10	31	29	14	
	170. 2/123. 0		51	33	10	
leuco crystal violet	374. 2/239. 0[b]	11. 1	41	31	14	D6-leuco crystal violet
	374. 2/358. 1		41	33	18	
leuco malachite green	331. 2/315. 3[b]	12. 5	36	39	12	D6-leuco malachite green
	331. 2/239. 1		36	39	4	
dehydro-17a-methyltestosterone(methandienone)	301. 4/121. 2[b]	11. 7	38	42	12	
	301. 4/149		38	36	4	
methyltestosterone	303. 2/97[b]	12	51	31	8	
	303. 2/108. 9		31	31	10	
metronidazole	172/128[b]	6. 7	36	39	4	
	172/82		36	39	12	
malachite green	329. 1/313. 3[b]	10. 7	41	29	6	D5-malachite green
	329. 1/208. 3		36	61	4	
nandrolone 17-propionate	331. 4/257. 4[b]	13. 2	56	65	16	
	331. 4/275. 0		56	37	12	

Table C. 1 (continued)

Compound[a]	Ion pairs Q1/Q3(m/z)	Retention time min	Declustering potential (DP)/ V	Collision energy (CE)/ V	Collision cell exit potential (CXP)/ V	IS Standard
nandrolone	275/109[b]	11.6	36	39	12	
	275/257		56	65	16	
ractopamine	302.1/164.1[b]	8.7	51	27	6	D5-ractopa mine
	302.1/283.9		36	39	4	
ronidazole	201/140[b]	7	36	39	12	D3-ronidazole
	201/55		56	65	16	
salbutamol	240.1/222[b]	6.7	56	65	16	D3-salbutamol
	240.1/148		56	37	12	
terbutaline	226.1/152.1[b]	6.6	36	39	4	
	226.1/170		36	39	12	
testosterone propionate	345.4/97.1[b]	13.6	41	33	18	
	345.4/109.1		41	31	14	
testostrone	289.3/96.9[b]	11.8	31	29	14	
	289.3/108.9		51	33	10	
tulobuterol	228.2/172[b]	9.6	61	45	16	
	228.2/153.8		41	31	14	
triamicinolone	395.4/225.1[b]	10.5	31	31	10	
	395.4/357.4		31	29	14	
triamcinolone acetonide	435.2/338.9[b]	11.3	51	33	10	
	435.2/396.9		51	37	12	
dienestrol	265.1/92.9[b]	9.6	−95	−35	−15	D8-dienestro
	265.1/249		−95	−35	−15	
diethylstilbestrol	267/250.9[b]	9.5	−115	−39	−13	
	267/237		−115	−46	−13	
hexestrol	269/134[b]	9.6	−75	−22	−11	
	269/119		−75	−42	−11	
D8-dienestrol	275/259	9.4	−108	−36	−13	
D5-chloramphenicol	326/157.1		−51	−24	−10	
zearalenone	317.1/175[b]	9.7	−101	−32	−5	
	317.1/131		−51	−40	−5	
α-zearalenol	319.1/301.1[b]	8.8	−111	−30	−5	
	319.1/275.2		−111	−29	−5	

Table C. 1 (continued)

Compound[a]	Ion pairs Q1/Q3(m/z)	Retention time min	Declustering potential (DP)/ V	Collision energy (CE)/ V	Collision cell exit potential (CXP)/ V	IS Standard
β-zearalenol	319.1/301.1[b]	8.3	−111	−42	−5	
	319.1/275.2		−111	−29	−5	
zearalanone	319.1/301.1[b]	9.6	−111	−42	−5	
	319.1/275.2		−111	−29	−5	
chloramphenicol	321/152[b]	6.8	−65	−25	−7	D5-chloram-phenicol
	321/257		−101	−42	−5	
α-zeranol	321/227.2[b]	8.7	−101	−29	−5	
	321/303.4		−101	−42	−7	
β-zeranol	321/227.2[b]	8.2	−101	−29	−5	
	321/303.4		−101	−42	−7	

Non-commercial statement: The equipments and their types involved in the standard method are not related to commercial aims, and it is encouraged to use equipments of diffierent corporation or different type.

[a] According to the English name of compounds initials sort.

[b] quantitative ion pairs.

Annex D
(informative annex)
LC-ms/ms

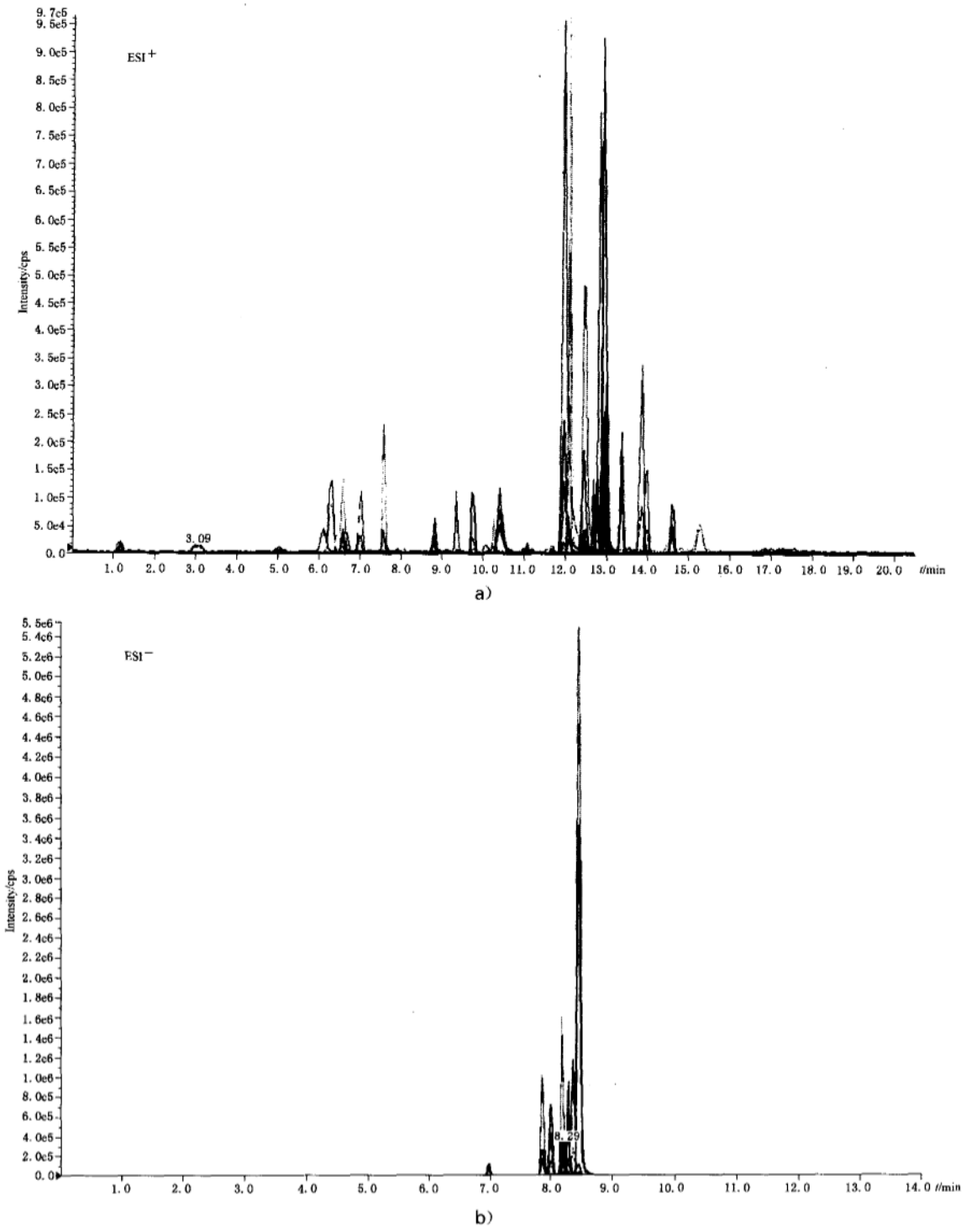


Figure D. 1—Total-ion chromatograms of 44 target compounds in positive and negative mode.

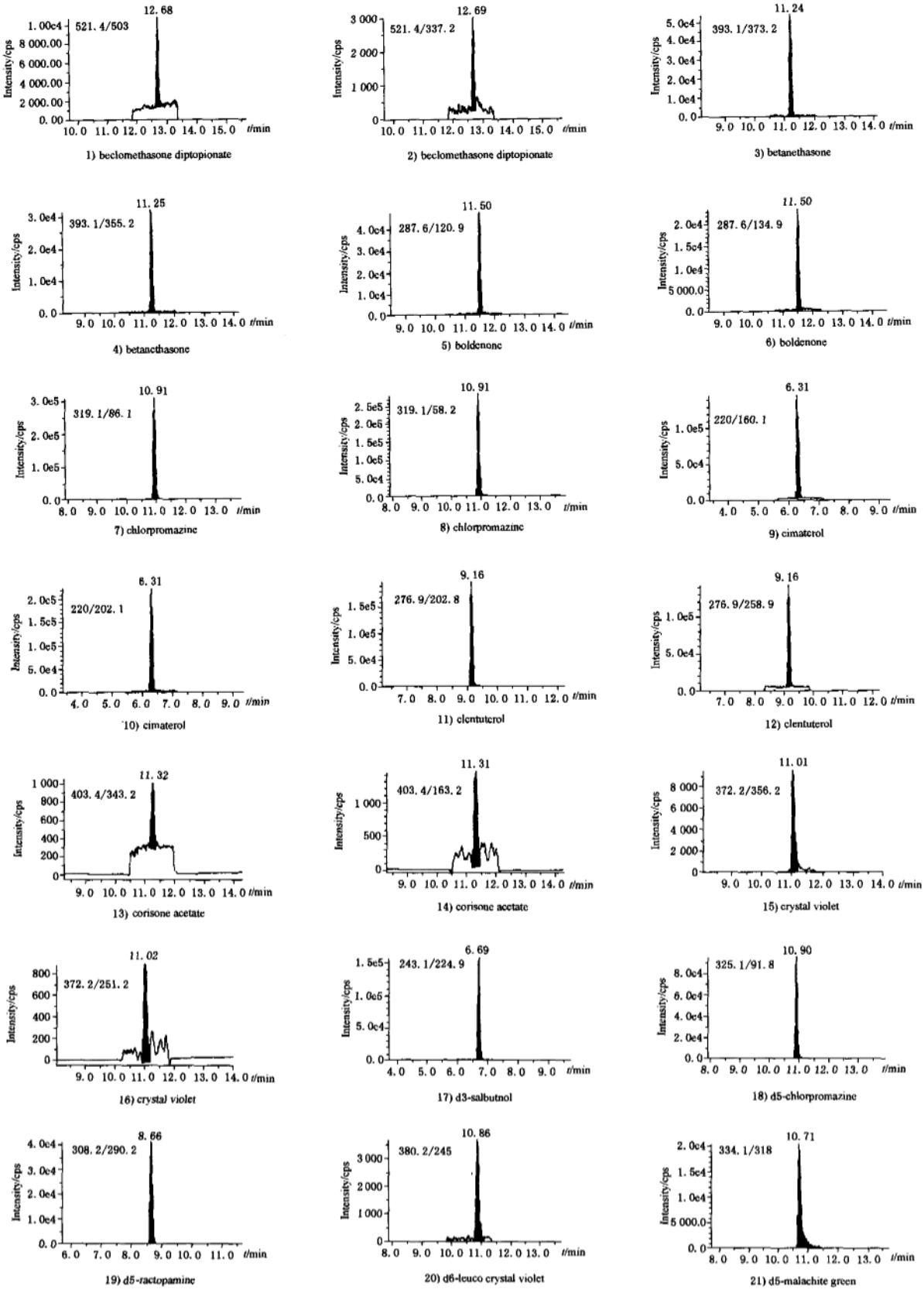


Figure D. 2—MRM chromatograph of chuemical standard

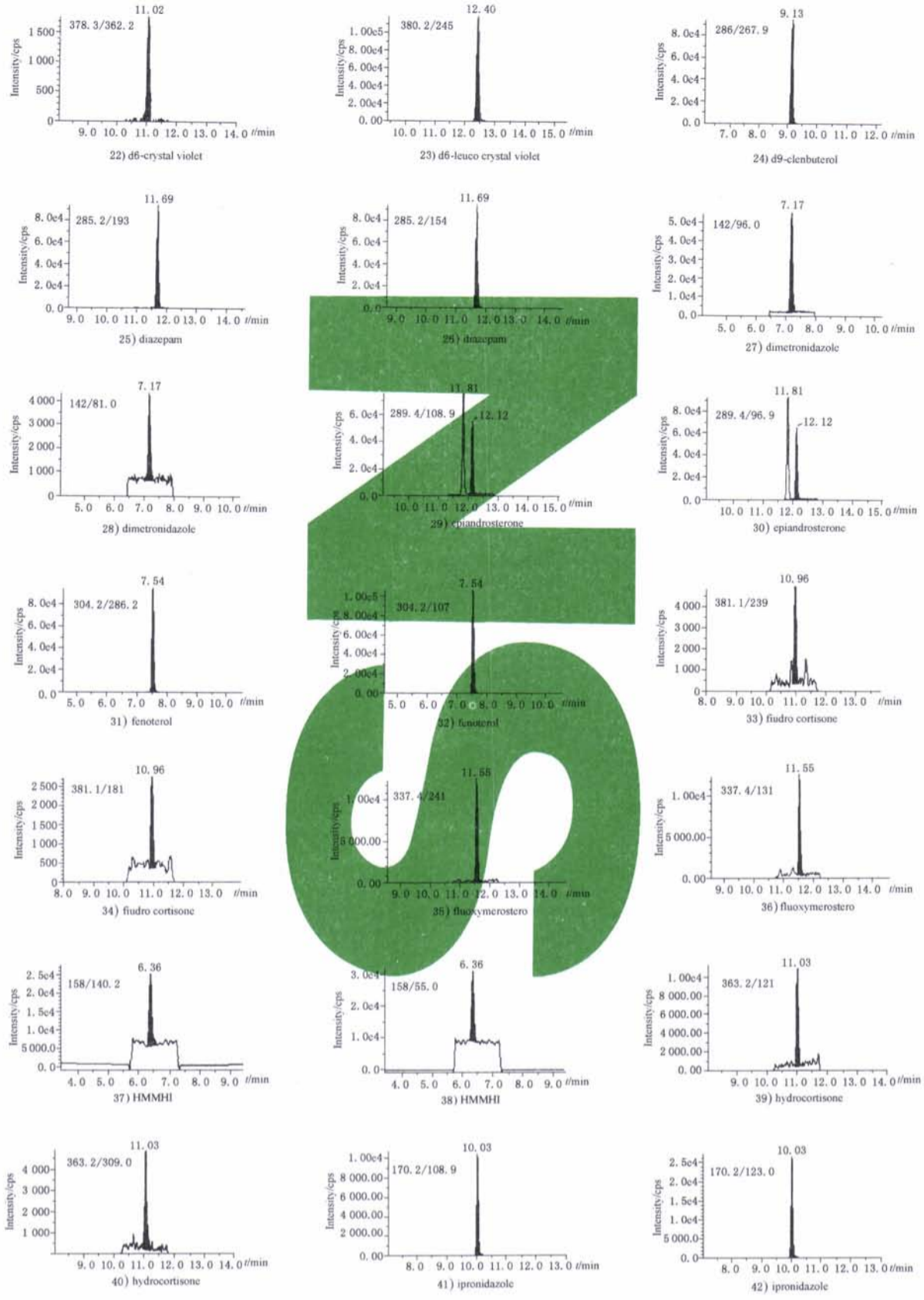


Figure D.2 (continued)

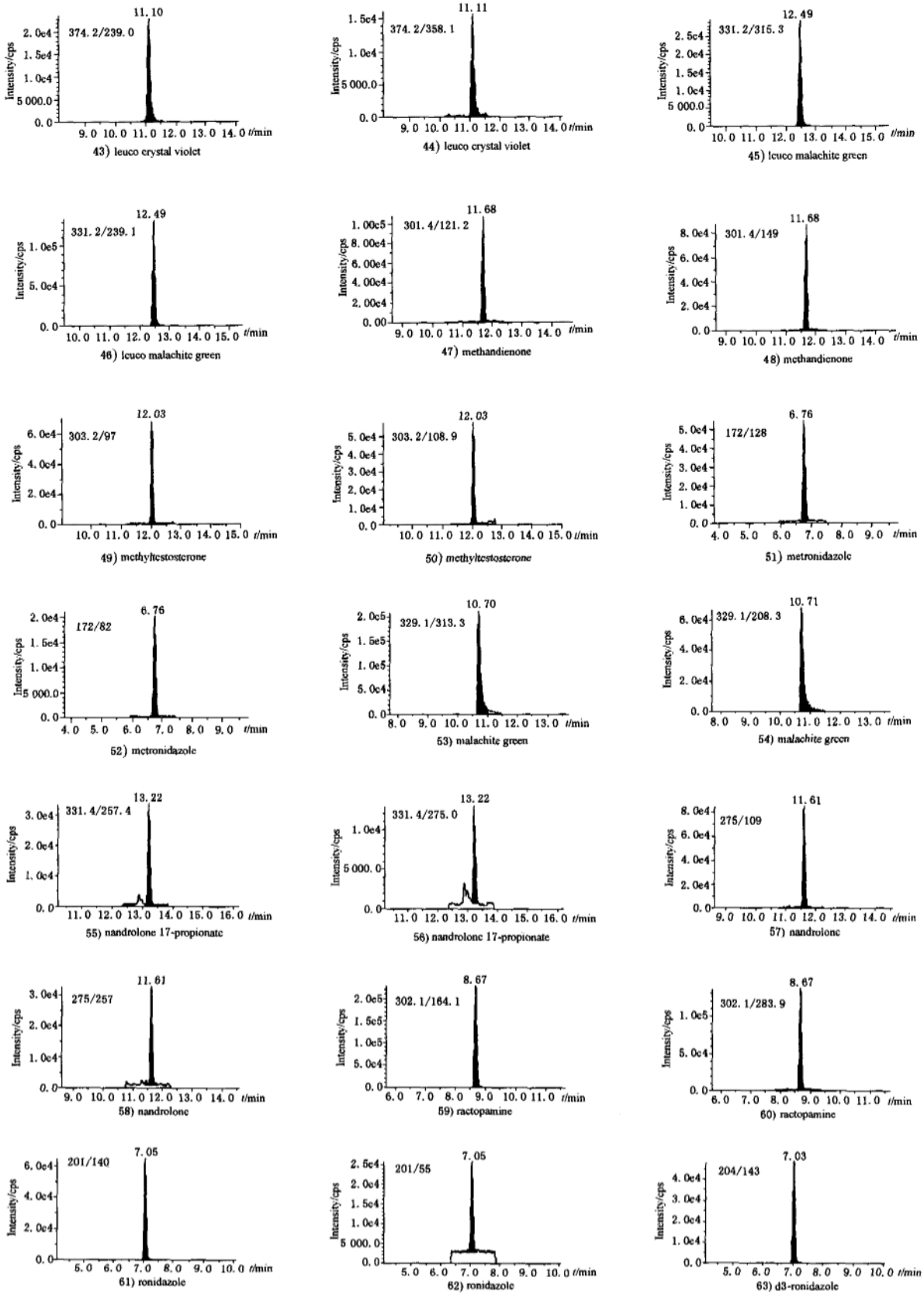


Figure D.2 (continued)

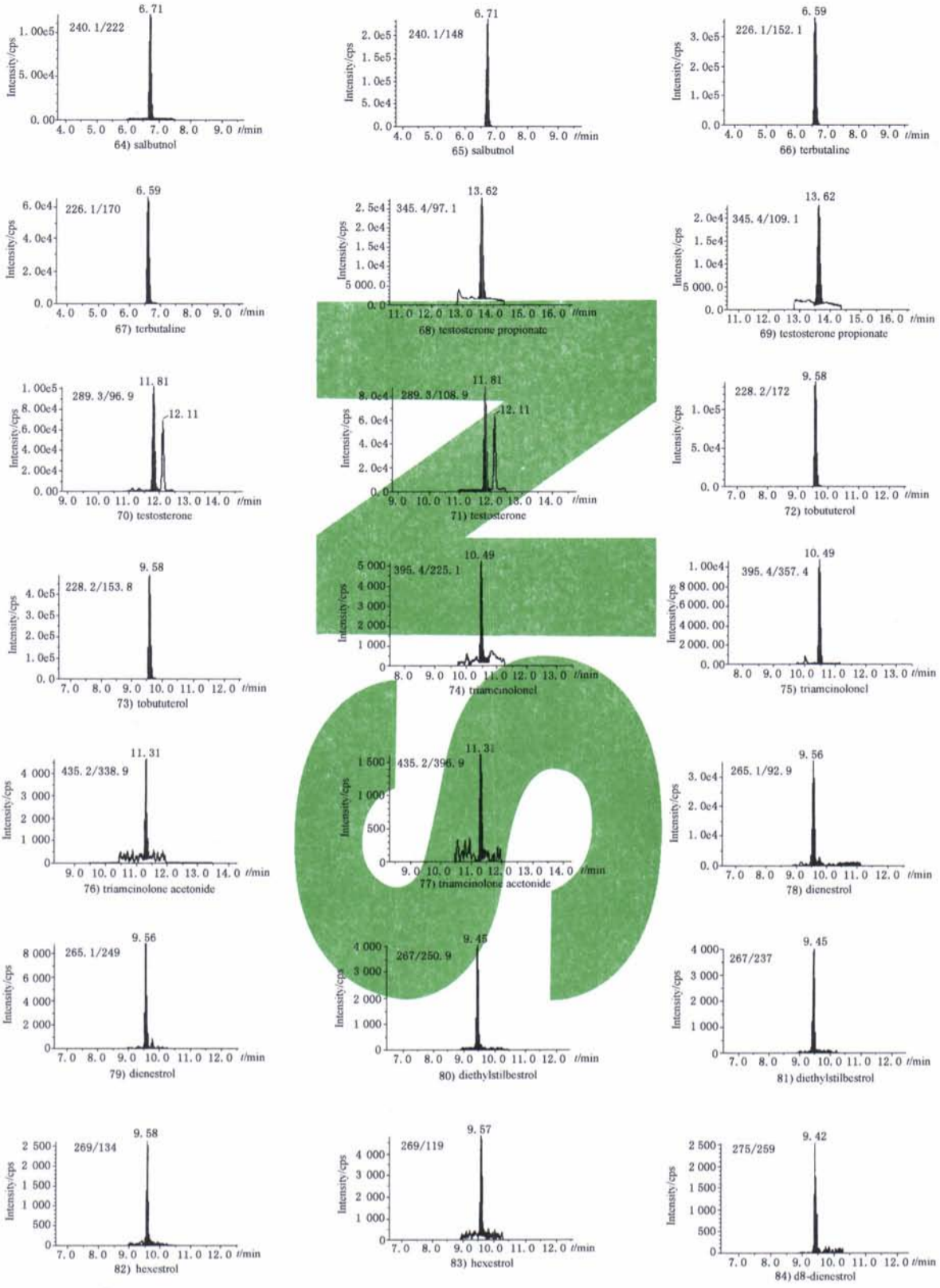


Figure D.2 (continued)

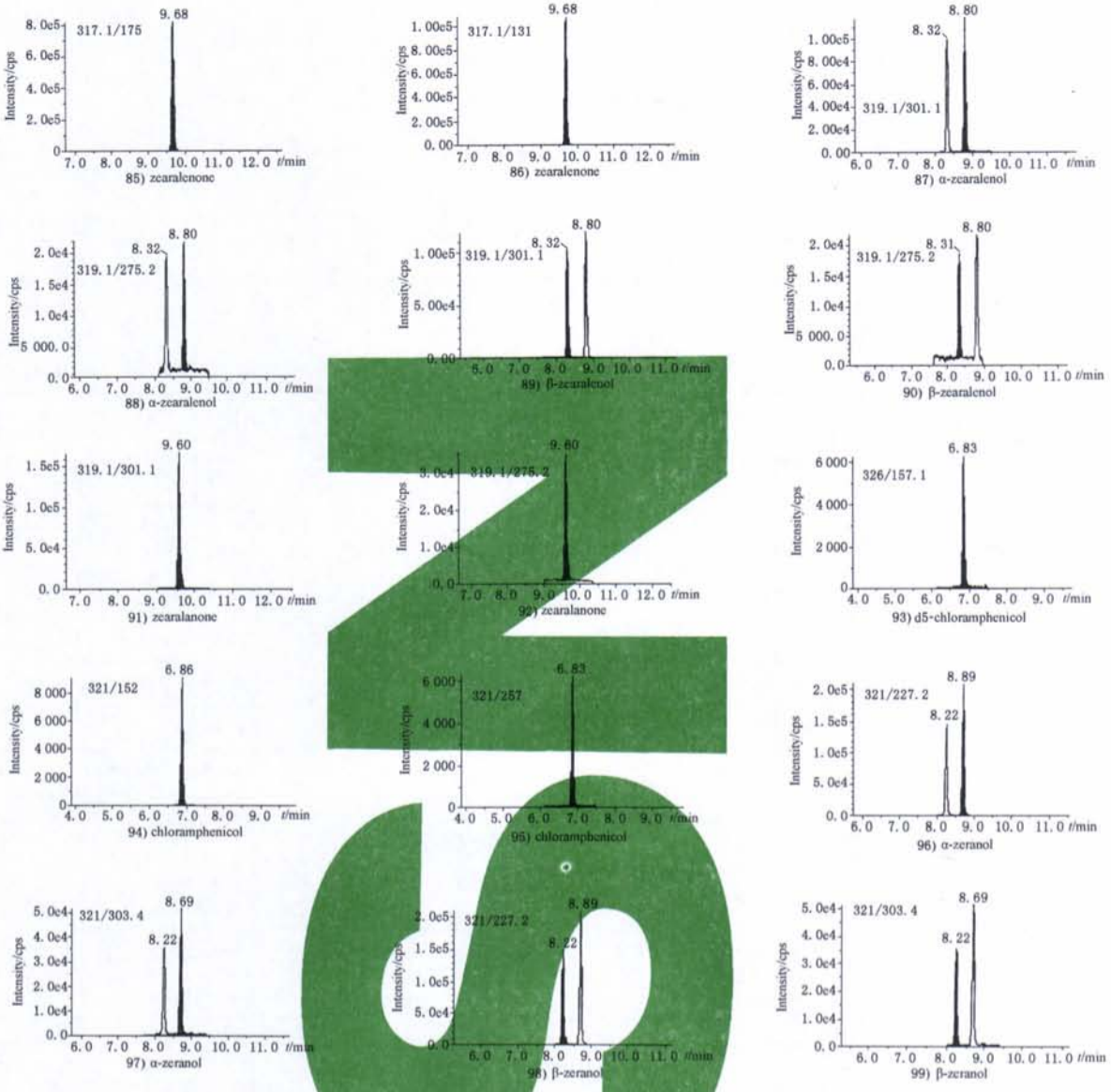


Figure D.2 (continued)

Annex E
(informative annex)
Linit determination

Table E. 1—Limit determination for milk sample

No.	Compound		Limit determination μg/kg	No.	Compound		Limit determination μg/kg
1	β-agonisits	cimaterol	0.5	16	Glucocorticoids	triamcinolone acetonide	1
2		cimaterol	0.5				
3		fenoterol	1	17	Resorcylic acid lactones	zearalenone	0.5
4		ractopamine	0.5	18		α-zearalenol	1
5		salbutamol	0.5	19		β-zearalenol	1
6		terbutaline	0.5	20		zearalanone	1
7		tulobuterol	0.5	21		α-zeranol	1
8	Androgens	boldenone	1	22		β-zeranol	1
9		epiandrosterone	1	23	Nitroimidazoles	dimetronidazole	0.5
10		dehydro-17 a-methyltest rosterone	1	24		ipronidazole	0.5
				25		metronidazole	0.5
				26		ronidazole	0.5
11		nandrolone	1	27	Estrogens	dienestrol	1
12		testostrone	1	28		diethylstilbestrol	1
13	Glucocorticoids	beclomethasone dipropionate	1	29		hexestrol	1
				30	Sedatives	chlorpromazine	0.5
14		betamethasone	0.5	31		diazapam	0.5
15		triamicinolone	0.5	32	Chloramphenicol	chloramphenicol	0.05

Table E. 2—Limit determination for liver sample

No.	Compound		Limit determination μg/kg	No.	Compound		Limit determination μg/kg
1	β-agonists	cimaterol	0.5	6	β-agonists	tulobuterol	0.5
2		cimaterol	0.5	7	Androgens	boldenone	1
3		ractopamine	0.5	8		epiandrosterone	0.5
4		salbutamol	0.5	9		methyltestosterone	1
5		terbutaline	0.5	10		nandrolone	1

Table E. 2 (continued)

No.	Compound		Limit determination μg/kg	No.	Compound		Limit determination μg/kg
11	Androgens	testostrone	1	22	Nitroimidazoles	dimetronidazole	0. 5
12	Glucocorticoids	beclomethasone dipropionate	1	23		ipronidazole	0. 5
				24		metronidazole	1
13		betamethasone	1	25		ronidazole	0. 5
14		triamicinolone	1	26	Estrogens	dienestrol	1
15		triamcinolone acetonide	1	27		diethylstilbestrol	1
				28		hexestrol	1
16	Resorcylic acid lactones	zearalenone	0. 5	29	Sedatives	chlorpromazine	0. 5
17		α-zearalenol	1	30		diazapam	0. 5
18		β-zearalenol	1	31	chloramphenicol	chloramphenicol	0. 05
19		zearalanone	0. 5				
20		α-zeranol	1				
21		β-zeranol	1				

Table E. 3—Limit determination for chicken sample

No.	Compound		Limit determination μg/kg	No.	Compound		Limit determination μg/kg
1	β-agonists	cimaterol	0. 5	13	Glucocorticoids	beclomethasone dipropionate	1
2		cimaterol	0. 5				
3		fenoterol	1	14		betamethasone	0. 5
4		ractopamine	0. 5	15		triamicinolone	0. 5
5		salbutamol	0. 5	16		triamcinolone acetonide	1
6		terbutaline	0. 5				
7		tulobuterol	0. 5	17	Resorcylic acid lactones	zearalenone	0. 5
8	Androgens	boldenone	1	18		α-zearalenol	1
9		epiandrosterone	1	19		β-zearalenol	1
10		dehydro-17 a-methyltest rosterone	1	20		zearalanone	1
				21		α-zeranol	1
				22		β-zeranol	1
11		nandrolone	1	23	Nitroimidazoles	dimetronidazole	0. 5
12		testostrone	1	24		ipronidazole	0. 5

Table E. 3 (continued)

No.	Compound		Limit determination μg/kg	No.	Compound		Limit determination μg/kg
25	Nitroimidazoles	metronidazole	0. 5	29	Estrogens	hexestrol	1
26		ronidazole	0. 5	30	Sedatives	chlorpromazine	0. 5
27	Estrogens	dienestrol	1	31		diazapam	0. 5
28		diethylstilb estrol	1	32	Chloramphenicol	chloramphenicol	0. 05

Table E. 4—Limit determination for pork sample

No.	Compound		Limit determination μg/kg	No.	Compound		Limit determination μg/kg
1	β-agonists	cimaterol	0. 5	16	Glucocorticoids	triamcinolone acetonide	1
2		cimaterol	0. 5				
3		fenoterol	1	17	Resorcylic acid lactones	zearalenone	0. 5
4		ractopamine	0. 5	18		α-zearalenol	1
5		salbutamol	0. 5	19		β-zearalenol	1
6		terbutaline	0. 5	20		zearalanone	1
7		tulobuterol	0. 5	21		α-zeranol	1
8	Androgens	boldenone	1	22		β-zeranol	1
9		epiandrosterone	1	23	Nitroimidazoles	dimetronidazole	0. 5
10		dehydro-17 a-methyltest rosterone	1	24		ipronidazole	0. 5
				25		metronidazole	0. 5
				26		ronidazole	0. 5
11		nandrolone	1	27	Estrogens	dienestrol	1
12		testostrone	1	28		diethylstilbestrol	1
13	Glucocorticoids	beclomethasone dipropionate	1	29		hexestrol	1
				30	Sedatives	chlorpromazine	0. 5
14		betamethasone	0. 5	31		diazapam	0. 5
15		triamicinolone	0. 5	32	Chloramphenicol	chloramphenicol	0. 05

Table E. 5—Limit determination for fish sample

No.	Compound		Limit determination μg/kg	No.	Compound		Limit determination μg/kg
1	β-agonists	cimaterol	0. 5	23	Glucocorticoids	triamcinolone acetonide	1. 0
2		cimaterol	0. 5				
3		fenoterol	0. 5	24	Resorcylic acid lactones	zearalenone	0. 5
4		ractopamine	0. 5	25		α-zearalenol	0. 5
5		salbutamol	0. 5	26		β-zearalenol	0. 5
6		terbutaline	0. 5	27		zearalanone	0. 5
7		tulobuterol	0. 5	28		α-zeranol	0. 5
8	Androgens	boldenone	0. 5	29		β-zeranol	1
9		epiandrosterone	0. 5	30	Nitroimidazoles	dimetronidazole	0. 5
10		fluoxymesterone	1	31		ipronidazole	0. 5
11		dehydro-17 a-methyltestrosterone	0. 5	32		metronidazole	0. 5
				33		ronidazole	0. 5
				34		hmmni	1. 0
12		methyltestosterone	1	35	Estrogens	dienestrol	1
13		nandrolone 17-propionate	0. 5	36		diethylstibestrol	1
				37		hexestrol	1
14		nandrolone	0. 5	38	Sedatives	chlorpromazine	0. 5
15		testosterone propionate	1	39		diazapam	0. 5
				40	Chloramphenicol	chloramphenicol	0. 05
16		testostrone	1	41	Triphenylmethanes	malachite green	0. 5
17	Glucocorticoids	beclomethasone dipropionate	1. 0	42		leuco malachite green	0. 5
18		betamethasone	0. 5	43		crystal violet	0. 5
19		cortisone acetate	1. 0	44		leuco crystal violet	0. 5
20		fludrocortisone	1. 0				
21		hydrocortisone	1. 0				
22		triamicinolone	1. 0				

Annex F
(informative annex)
Recovery range

Table F. 1—Recovery range for milk sample($n=6$)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
beclomethasone dipropionate	1	70. 3～84. 1	ipronidazole	0. 5	92～105. 2
	2	90. 5～104. 5		1	88. 9～104
	4	92. 25～103. 75		2	86. 5～92. 5
betamethasone	0. 5	95. 6～108. 8	methandienone	1	83. 4～102
	1	97. 5～113		2	94～104. 5
	2	93. 5～116		4	89. 25～108. 75
boldenone	1	96～112	metronidazole	0. 5	72. 4～114
	2	88～112		1	90. 4～113
	4	97. 75～114. 5		2	78. 5～115
chlorpromazine	0. 5	81. 6～100. 4	nandrolone	1	95. 6～114
	1	83～111		2	93. 5～112. 5
	2	84～100		4	106. 75～118. 5
cimaterol	0. 5	75. 6～118	ractopamine	0. 5	91. 6～103. 8
	1	78. 6～114		1	87. 4～103
	2	78. 5～119		2	91. 5～99. 5
clenbuterol	0. 5	98. 2～110. 6	ronidazole	0. 5	73. 4～103. 6
	1	92. 6～99. 9		1	92. 1～117
	2	93～100. 5		2	91. 5～118. 5
diazapam	0. 5	63. 8～99. 8	salbutamol	0. 5	80. 8～112. 8
	1	83. 3～113		1	64. 3～104
	2	72～110		2	65. 5～103
dimetronidazole	0. 5	67. 4～100. 4	terbutaline	0. 5	75～107. 2
	1	69. 7～86. 8		1	76. 8～117
	2	76. 5～102		2	98～111
epiandrosterone	1	89. 2～111	testostrone	1	84. 7～98. 3
	2	100～111. 5		2	91～109
	4	103. 5～108. 5		4	99～109
fenoterol	1	83. 1～98	tulobuterol	0. 5	70～118. 2
	2	85. 2～96. 3		1	102～107
	4	81. 6～99. 2		2	99. 5～104

Table F. 1 (continued)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
triamicinolone	0.5	70～115.8	α-zearalenol	1	69.6～99.1
	1	97.3～117		2	85～110.5
	2	82～113.5		4	100～111.5
triamcinolone acetonide	1	89.5～116	β-zearalenol	1	88.9～102
	2	97～118.5		2	100～108
	4	102～114.75		4	91～110.25
dienestrol	1	102～118	zearalanone	1	72～92.1
	2	104～117.5		2	89～112.5
	4	90.3～114		4	92.25～117.25
diethylstilbestrol	1	76.1～108	chloramphenicol	0.05	77.6～106
	2	66.5～99.2		0.1	94.2～116
	4	76.8～106.25		0.2	95.5～124.5
hexestrol	1	63.9～91.2	α-zeranol	1	91.5～110
	2	71.5～112		2	103～124
	4	80～118.75		4	99.5～118.25
zearalenone	0.5	72.8～95.6	β-zeranol	1	89.5～106
	1	82.7～101		2	101～119
	2	91～118.5		4	96～114.25

Table F. 2—Recovery range for liver sample($n = 6$)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
betanethasone	1	102～120	clentuterol	0.5	83～105
	2	99～112		1	66～108
	4	98.1～104		2	72.5～78.5
bldenone	1	89.8～111	diazepam	0.5	91.6～115
	2	82～97.5		1	93.7～119
	4	82.3～95.5		2	86.5～110
chlorpromazine	0.5	96～116	dimetronidazole	1	89.3～104
	1	93.7～109		2	87～95.5
	2	86.5～110		4	61.8～74.5
cimaterol	0.5	99.5～104	epiandrosterone	0.5	75～104
	1	105～118		1	82.1～107
	2	102～110		2	86～102

Table F. 2 (continued)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
hydrocortisone	1	76. 8～93. 1	triamcinolonel	1	85. 8～102
	2	76. 4～99. 5		2	74. 5～98. 5
	4	85. 5～101		4	63. 3～96. 8
ipronidazole	0. 5	94. 2～102	triamcinolone acetonide	1	76. 5～93. 3
	1	83. 8～94. 9		2	73. 5～85
	2	89～98		4	66. 5～85. 8
methyltestosterone	1	88. 6～106	dienestrol	1	82. 3～117
	2	92～104		2	75～109
	4	93. 7～112		4	72～117
metronidazole	1	87. 3～91. 9	diethylstilbestrol	1	101～118
	2	85. 5～101		2	83. 3～118
	4	78. 3～94. 5		4	84～119
nandrolone	1	91～115	hexestrol	1	79. 5～116
	2	99. 5～105		2	70. 5～119
	4	85～95. 5		4	74. 5～93. 3
ractopamine	0. 5	109～119	zearalenone	0. 5	99. 6～115
	1	98. 8～108		1	88. 2～111
	2	94. 5～98. 5		2	85. 1～93. 7
ronidazole	0. 5	85. 1～96. 1	α-zearalenol	1	81～119
	1	82. 3～99. 2		2	81～96. 5
	2	90. 6～105		4	84. 8～113
salbutnol	0. 5	76～106	β-zearalenol	1	101～115
	1	70. 1～88. 2		2	83～108
	2	80. 5～95. 5		4	71～84
terbutaline	0. 5	96. 8～115	zearalanone	0. 5	81. 5～109
	1	96. 1～118		1	71. 2～107
	2	101～114		2	92～108
testosterone	1	75. 4～93. 7	chloramphenicol	0. 1	87. 2～112
	2	83～99		0. 2	86～104
	4	91. 5～118		0. 4	69～90
tobututerol	0. 5	101～117	α-zeranol	1	70～103
	1	95～119		2	100～119
	2	108～115		4	102～118
			β-zeranol	1	79. 7～126
				2	69. 3～105
				4	79. 1～119

Table F. 3—Recovery range for chicken sample($n = 6$)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
beclomethasone dipropionate	1	79. 2～98. 8	dehydro-17a-methyltestrosterone	1	88. 1～104
	2	87. 5～101		2	95. 5～106
	4	89. 8～98. 5		4	96. 1～98. 1
betamethasone	0. 5	92. 4～107	metronidazole	0. 5	94. 4～102
	1	99. 1～113		1	92. 8～97. 5
	2	108～116		2	101～104
boldenone	1	79. 9～110	nandrolone	1	101～110
	2	94. 1～118		2	101～119
	4	101～119		4	101～118
chlorpromazin	0. 5	98. 2～116	ractopamine	0. 5	97. 6～115
	1	86. 3～111		1	88. 6～103
	2	102～116		2	86. 5～116
cimaterol	0. 5	85. 1～104	ronidazole	0. 5	86. 1～102
	1	90. 7～117		1	70. 2～115
	2	97～113		2	111～115
cimaterol	0. 5	86. 4～103	salbutamol	0. 5	86. 4～111
	1	90. 1～107		1	86. 5～96. 1
	2	90～106		2	86. 5～92. 5
diazapam	0. 5	87. 8～99. 2	terbutaline	0. 5	84. 1～88. 6
	1	81. 5～92. 7		1	90. 9～96. 6
	2	97. 1～110		2	88. 5～93. 1
dimetronidazole	0. 5	91. 6～101	testostrone	1	89. 7～98. 2
	1	99. 6～106		2	103～112
	2	109～112		4	99. 5～109
epiandrosterone	1	100～108	tulobuterol	0. 5	89. 8～103
	2	107～117		1	90. 2～101
	4	99. 8～114		2	100～104
fenoterol	1	76. 4～93. 1	triamicinolone	0. 5	86. 3～102
	2	84. 5～99. 5		1	90. 2～106
	4	86～99. 5		2	102～117
ipronidazole	0. 5	88. 4～105	triamcinolone acetonide	1	91. 9～116
	1	94. 2～102		2	95. 1～106
	2	99. 5～114		4	85. 5～102

Table F. 3 (continued)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
dienestrol	1	85. 4～112	β-zearalenol	1	99. 1～116
	2	78. 1～97. 5		2	101～119
	4	67. 5～107		4	93. 2～113
diethylstilbestrol	1	104～119	zearalanone	1	66. 8～83. 9
	2	75. 2～119		2	80. 5～117
	4	89. 2～114		4	67. 8～100
hexestrol	1	65. 1～94. 5	chloramphenicol	0. 05	70. 8～88. 1
	2	76. 1～114		0. 1	81. 1～97. 6
	4	70. 1～113		0. 2	86. 1～99. 1
zearalenone	0. 5	90. 2～104	α-zeranol	1	71. 7～99. 1
	1	78. 1～96. 8		2	94. 5～110
	2	96. 1～120		4	80. 2～116
α-zearalenol	1	75. 1～87. 1	β-zeranol	1	81. 5～101
	2	80. 5～117		2	93. 1～114
	4	84. 2～108		4	85. 2～111

Table F. 4—Recovery range for pork sample($n = 6$)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
beclomethasone dipropionate	1	89. 2～112	cimaterol	0. 5	90～116. 6
	2	98. 5～117		1	95. 1～106
	4	83. 25～117. 75		2	93. 5～108
betamethasone	0. 5	102～115	diazapam	0. 5	98. 2～107. 4
	1	102～117		1	87. 9～114
	2	103～117. 5		2	90～97
boldenone	1	101～117	dimetronidazole	0. 5	82. 6～97. 8
	2	80. 5～109		1	64. 7～72. 9
	4	94. 75～113. 5		2	60～78. 75
chlorpromazin	0. 5	71. 4～113. 8	epiandrosterone	1	91. 9～115
	1	73. 6～89. 5		2	91. 75～108. 25
	2	87. 5～110		4	110. 75～117. 75
cimaterol	0. 5	104. 4～109	fenoterol	1	76. 3～89. 1
	1	80. 9～92. 6		2	82. 1～96. 4
	2	69. 5～119		4	86. 4～106

Table F.4 (continued)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
ipronidazole	0.5	91～109.4	triamcinolone acetonide	1	74.3～84.5
	1	93.8～107		2	93.5～116
	2	85.5～103.75		4	96.75～113
dehydro-17a-methyltestrosterone	1	71.2～110	dienestrol	1	89.4～104
	2	79.5～100.25		2	83.5～108.5
	4	101～113.75		4	100.25～115.75
metronidazole	0.5	88.4～103.8	diethylstilbestrol	1	77.5～110
	1	79.7～105		2	89.5～108.5
	2	60.5～104.75		4	99.75～117.75
nandrolone	1	80～112	hexestrol	1	65～97.5
	2	92.4～108		2	63.25～118.25
	4	101～116.75		4	74.75～102.25
ractopamine	0.5	99.2～111.8	zearalenone	0.5	91.4～107
	1	90～93.9		1	95.7～117
	2	80～108		2	104～117.5
ronidazole	0.5	85.6～112.8	α-zearalenol	1	88.5～119
	1	84.9～105		2	80.5～99.5
	2	84.5～104.25		4	67～79.75
salbutamol	0.5	93.2～109.6	β-zearalenol	1	65.1～105
	1	95～105		2	69～106
	2	89.5～107		4	67.5～77
terbutaline	0.5	103～118.2	zearalanone	1	83.1～95.2
	1	99.3～110		2	86.1～106
	2	99.5～117		4	92.3～105
testostrone	1	92～118	chloramphenicol	0.05	67.2～88
	2	91.5～110		0.1	81.5～95.4
	4	100～114.75		0.2	93.5～110
tulobuterol	0.5	92.8～103.8	α-zeranol	1	87～117
	1	96.7～111		2	89～106
	2	84～115		4	88～104
triamicinolone	0.5	93.8～114.6	β-zeranol	1	71.8～79.1
	1	96.2～119		2	65～107.5
	2	91.5～114		4	58.2～78.5

Table F. 5—Recovery range for fish sample($n=6$)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
beclomethasone dipropionate	1	89. 7～103	fenoterol	0. 5	78. 2～101
	2	81～100. 5		1	86. 1～103
	4	80. 25～98. 75		2	79. 2～105
betamethasone	0. 5	102. 2～114. 6	fludrocortisone	1	85. 6～112
	1	95. 1～101		2	73. 5～99. 5
	2	73～96. 5		4	82. 5～93. 5
boldenone	0. 5	93. 8～108. 2	fluoxymesterone	1	82. 9～113
	1	80～101		2	93～108. 5
	2	78. 5～100. 5		4	78. 5～94. 75
chlorpromazin	0. 5	101. 4～109. 6	1-methyl-5-nitro-1H-imidazole (HMMNI)	1	93. 7～101
	1	93. 2～104		2	83. 5～106
	2	87～97		4	80. 75～90. 75
cimaterol	0. 5	61～94. 6	hydrocortisone	1	70. 9～110
	1	60. 5～92. 2		2	76. 5～110. 5
	2	76. 5～90. 5		4	86. 25～103. 5
cimaterol	0. 5	99. 6～110	ipronidazole	0. 5	106～117. 8
	1	93. 1～101		1	94. 1～118
	2	94～99. 5		2	86. 5～105. 5
cortisoneacetate	1	80. 4～107	leuco crystal violet	0. 5	68. 2～110. 4
	2	84. 5～100		1	82. 7～114
	4	82. 5～95. 25		2	90. 1～119
crystal violet	0. 5	100～119. 8	leuco malachite green	0. 5	102～119. 8
	1	85. 3～105		1	82. 8～98
	2	82～108. 5		2	77. 5～97
diazapam	0. 5	84～108	dehydro-17a-methyltestrosterone	0. 5	93. 2～112. 2
	1	83. 5～92. 1		1	81～92. 7
	2	76. 5～107		2	83. 5～98. 5
dimetronidazole	0. 5	102～118. 6	methyltestosterone	1	80. 7～104
	1	95. 5～109		2	67. 5～99. 5
	2	91. 5～111		4	84～96. 2
epiandrosterone	0. 5	94. 2～110	metronidazole	0. 5	70. 6～106. 6
	1	86～113		1	69. 6～82. 3
	2	77～103. 5		2	69～95

Table F. 5 (continued)

Compound	Spiked concentration μg/kg	Recovery range %	Compound	Spiked concentration μg/kg	Recovery range %
malachite green	0. 5	84. 4～103. 2	triamcinolone acetonide	1	81. 2～107
	1	76. 5～95. 2		2	83～111. 5
	2	64. 5～99		4	74. 25～85. 75
nandrolone	0. 5	88. 2～103	dienestrol	1	79. 7～105
	1	85. 2～110		2	91～108
	2	83～102		4	74. 5～108. 25
ractopamine	0. 5	97. 8～114	diethylstilbestrol	1	85. 1～98. 7
	1	90. 6～102		2	63. 5～108. 5
	2	79～106		4	56～91
ronidazole	0. 5	95～107	hexestrol	1	71. 8～95. 5
	1	86. 9～94. 7		2	63. 5～94
	2	87. 5～106. 5		4	67. 5～99
nandrolone	0. 5	103～110	zearalenone	0. 5	96. 8～118. 6
	1	94. 8～106		1	75. 3～107
	2	90. 5～99. 5		2	72～94
salbutamol	0. 5	84. 2～117. 2	α-zearalenol	0. 5	83. 4～107
	1	70. 8～108		1	81. 6～91. 6
	2	89～108		2	79. 5～95. 5
terbutaline	0. 5	78. 6～115	β-zearalenol	0. 5	88. 6～109. 8
	1	68. 2～91. 3		1	81. 6～101
	2	80. 5～94		2	74. 5～106
testosterone propionate	1	85. 2～115	zearalanone	0. 5	70. 3～99. 2
	2	85. 5～103		1	76. 2～96. 3
	4	91～114		2	83. 1～99. 3
testostrone	1	88. 7～106	chloramphenicol	0. 05	85. 6～114
	2	81～105. 5		0. 1	69. 6～119
	4	80. 5～90. 75		0. 2	68. 5～109
tulobuterol	0. 5	72. 8～94	α-zeranol	0. 5	101～111. 4
	1	86. 4～94. 2		1	86. 1～112
	2	86. 5～108		2	88. 5～100
triamicinolone	1	84. 9～114	β-zeranol	1	92. 4～116
	2	88～106		2	90. 5～100
	4	85. 75～106		4	89. 75～100