

LCMS-8050 定量测定抗疲劳饮料和补肾药酒中 90 种那非类物质

LCMSMS-391

摘要：本文建立了一种使用岛津超高效液相色谱仪 LC-30A 和三重四极杆质谱仪 LCMS-8050 联用测定抗疲劳饮料和补肾药酒中 90 种那非类物质的方法。采用外标法定量，方法线性范围为 0.1~50.0 ng/mL，相关系数大于 0.998。保留时间和峰面积的相对标准偏差分别在 0.02~0.34% 和 1.22~4.96% 之间。进样 5.0 μ L，检出限在 0.0007~0.1379 ng/mL 之间，定量限在 0.0021~0.4221 ng/mL 之间。抗疲劳饮料样品有 89 种化合物加标回收率在 81.6~113.5% 之间。药酒样品有 82 种化合物加标回收率在 80.2~111.9% 之间，有 4 种化合物加标回收率在 70.6~79.9% 之间。使用本方法检测了三个品牌的抗疲劳饮料，其中两个品牌检出西地那非（Sildenafil）。

关键词：超高效液相色谱 三重四极杆质谱 那非类物质 保健食品

那非类物质（Antifatigue drugs）是一种人体内 5 型磷酸二酯酶（PDE5）的抑制剂，可用于治疗男性勃起功能障碍。该类物质已知的副作用包括面部潮红、头晕、头痛、鼻塞和视觉异常等，严重的会导致死亡，是一种须在医生指导下服用的处方药。

近年来，随着化学合成技术的进步，一些具有 PDE5 抑制活性的那非类衍生物不断涌现，被一些不法分子添加至标示或暗示具有补肾壮阳、抗疲劳、改善免疫力等作用的食品中，对服用者的健康和生命安全造成严重威胁。我国《食品安全法》第三十八条规定，生产经营的食品中不得添加药品，但是可以添加按照传统既

是食品又是中药材的物质。那非类物质是处方药，在食品或保健食品等特殊食品中添加属于违法行为，必须予以打击。

这些那非类物质结构类似，存在多种同分异构体，给质谱检测带来挑战。故需要充分优化色谱方法，有效分离同分异构体，从而实现准确定量。

本文参考国家市场监督管理总局于 2018 年 7 月 2 日发布的《食品中那非类物质的测定》的食品补充检验方法，采用岛津三重四极杆液质联用仪 LCMS-8050，建立了食品中 90 种那非类物质的分析方法。供相关检测人员参考。

实验部分

1.1 仪器

本实验使用岛津超高效液相色谱仪 LC-30A 与三重四极杆质谱仪 LCMS-8050 联用系统。具体配置为 LC-30AD \times 2 输液泵，DGL-20A₅ 在线脱气机，SIL-30AC 自动进样器，CTO-20A 柱温箱，CBM-20A 系统控制器，LCMS-8050 三重四极杆质谱仪，LabSolutions (Version 5.93) 色谱工作站。

1.2 分析条件

液相色谱条件

色谱柱：Shim-pack GIST 2.1 mm I.D. \times
150 mm L., 2.0 μ m

流动相：A 相 -0.1% 甲酸；B 相 - 甲醇

洗针模式：进样前后洗针，External only（进样
针外壁清洗），Rinse Port

流速：0.3 mL/min

柱温：40 $^{\circ}$ C

进样体积：5 μ L

洗针液：甲醇 / 水 =1:1 (v:v)

洗脱方式：梯度洗脱，B 相初始浓度为 15%，时
间程序见表 1。

表1 梯度洗脱时间程序

Time(min)	Module	Command	Value
1.00	泵	B.Conc	50
16.00	泵	B.Conc	65
19.00	泵	B.Conc	98
22.00	泵	B.Conc	98
22.10	泵	B.Conc	15
25.00	控制器	Stop	

质谱条件

离子化模式：ESI，正负离子同时检测

干燥气流速：10.0 L/min

碰撞气：氩气 270 kPa

接口温度：300°C

雾化气流速：3.0 L/min

扫描模式：多反应监测 (MRM)

加热模块温度：400°C

DL 温度：250°C

加热气流速：10.0 L/min

MRM 参数：见表 2

表2 MRM参数

No.	英文名称	中文名称	CAS号	参考保留时间 (min)	前体离子	产物离子	Q1 Pre Bias(V)	CE(V)	Q3 Pre Bias(V)
1	Sildenafil	西地那非	139755-83-2	5.386	475.20	100.20* 283.20	-11 -11	-28 -39	-18 -19
2	Tadalafil	他达拉非	171596-29-5	9.395	390.10	135.00* 204.05	-30 -30	-23 -55	-14 -30
3	Imidazosagatriazinone	脱硫伐地那非	139756-21-1	19.110	313.15	285.10* 256.10	-11 -11	-25 -29	-30 -28
4	Gildenafil	伐地那非	147676-66-2	14.338	355.20	285.20* 327.20	-10 -10	-30 -25	-19 -16
5	Acetil acid	那非乙酰胺	147676-78-6	12.474	357.20	329.20* 285.20	-10 -10	-26 -30	-16 -20
6	Xanthoanthrafil	苯酰胺那非	1020251-53-9	7.596	390.20	151.10* 107.10	-11 -11	-20 -58	-16 -19
7	Aminotadalafil	氨基他达拉非	385769-84-6	7.569	391.10	204.10* 262.10	-14 -20	-60 -32	-21 -30
8	Chloropretadalafil	他达拉非甲基氯化物	171489-59-1	12.499	427.15	135.10* 274.10	-10 -12	-21 -33	-14 -30
9	Piperiacetildenafil	苯噻啶红地那非	147676-50-4	5.061	438.25	98.15* 297.20	-10 -10	-32 -37	-18 -20
10	Noracetildenafil	那红地那非	949091-38-7	4.814	453.25	97.10* 113.15	-10 -13	-31 -31	-18 -20
11	Carbodenafil	卡巴地那非	944241-52-5	4.221	453.30	339.20* 311.20	-10 -10	-24 -33	-17 -15
12	Pseudovardenafil	伪伐地那非	224788-34-5	16.629	460.2	151.15* 312.25	-13 -11	-42 -37	-16 -22
13	Norneosildenafil	那莫西地那非	371959-09-0	18.768	460.2	283.10* 299.20	-13 -13	-36 -37	-19 -21
14	N-Desethylvaridenafil	N-去乙基伐地那非	448184-46-1	4.976	461.20	151.10* 312.25	-13 -11	-43 -37	-15 -22
15	N-Desmethylsildenafil	N-去甲基西地那非	139755-82-1	5.308	461.20	283.10* 311.20	-13 -13	-38 -29	-19 -15
16	Acetildenafil	红地那非	831217-01-7	4.956	467.30	111.20* 127.20	-11 -13	-31 -31	-21 -13
17	Hydroxyacetildenafil	羟基红地那非	147676-56-0	4.755	483.25	127.15* 143.15	-11 -11	-30 -33	-23 -27
18	Avanafil	阿伐那非	330784-47-9	4.939	484.15	375.20* 155.10	-11 -11	-26 -43	-18 -16
19	Aildenafil	艾地那非	496835-35-9	5.733	489.20	99.10* 113.15	-11 -11	-35 -31	-22 -18

20	Homosildenafil	豪莫西地那非	642928-07-2	5.325	489.20	72.10 *	-11	-48	-18
						113.15	-11	-29	-26
21	Vardenafil	伐地那非	224785-90-4	5.009	489.20	151.10*	-11	-47	-15
						312.20	-14	-40	-22
22	Thiosildenafil	硫代西地那非	479073-79-5	10.631	491.15	299.05*	-30	-38	-15
						100.20	-30	-30	-20
23	Thiohomosildenafil	硫代豪莫西地那非	479073-80-8	10.760	505.25	113.20*	-24	-31	-21
						299.10	-24	-39	-20
24	Hydroxyvardenafil	羟基伐地那非	224785-98-2	4.973	505.20	151.10*	-20	-49	-15
						312.20	-20	-39	-15
25	Hydroxyhomosildenafil	羟基豪莫西地那非	139755-85-4	5.269	505.25	99.20*	-20	-39	-19
						129.20	-24	-29	-24
26	Udenafil	乌地那非	268203-93-6	6.261	517.25	283.15*	-20	-45	-19
						112.15	-20	-34	-21
27	Hydroxythiohomosildenafil	羟基硫代豪莫西地那非	479073-82-0	10.682	521.25	99.20*	-20	-40	-18
						129.20	-24	-31	-13
28	Norneovardenafil	那莫伐地那非	358390-39-3	10.395	357.15	151.10*	-10	-30	-16
						329.20	-10	-24	-16
29	Nitrodenafil	硝地那非	147676-99-1	17.791	358.20	284.20*	-10	-31	-19
						330.20	-10	-23	-23
30	Nortadalafil	去甲基他达拉非	171596-36-4	8.091	376.10	204.10*	-30	-56	-21
						262.10	-30	-29	-28
31	Chlorodenafil	氯地那非	1058653-74-9	15.832	389.10	361.20*	-11	-27	-18
						285.10	-11	-33	-20
32	Hydroxychlorodenafil	羟基氯地那非	1391054-00-4	14.566	391.20	313.20*	-11	-34	-22
						285.20	-11	-32	-20
33	N-Butyltadalafil	N-丁基他达拉非	171596-31-9	16.426	432.20	310.20*	-10	-17	-15
						135.10	-10	-24	-14
34	Desmethylcarbodenafil	去甲基卡巴地那非	147676-79-7	4.138	439.20	339.20*	-10	-23	-17
						311.20	-10	-33	-15
35	Descarbonsildenafil	去碳西地那非	1393816-99-3	4.794	463.20	283.20*	-11	-39	-19
						311.20	-11	-31	-22
36	Dimethylacetildenafil	二甲基红地那非	1290041-88-1	5.667	467.25	127.20*	-11	-31	-17
						166.10	-11	-53	-13
37	Dithio-desmethylcarbodenafil	二硫代去甲基卡巴地那非	1333233-46-7	11.548	471.25	371.20*	-13	-24	-18
						343.20	-11	-35	-24
38	Oxohongdenafil	酮红地那非	1446144-70-2	9.427	481.30	410.25*	-11	-31	-20
						297.20	-11	-44	-20
39	N-Octylnortadalafil	N-辛基去甲他达拉非	1173706-35-8	20.325	488.20	366.30*	-11	-20	-18
						169.10	-11	-44	-17
40	Dioxohongdenafil	双酮红地那非	1609405-33-5	8.771	495.20	127.20*	-11	-38	-23
						311.20	-11	-40	-22
41	Hydroxythiovardenafil	羟基硫代伐地那非	912576-30-8	8.749	521.20	167.10*	-20	-54	-17
						99.20	-20	-36	-19
42	Cyclopentynafil	环戊那非	1173706-34-7	5.971	529.20	98.20*	-20	-36	-18
						461.25	-20	-39	-23
43	Propoxyphenyl thiohydroxyhomosildenafil	丙氧苯基硫代羟基豪莫西地那非	479073-90-0	12.963	535.25	99.20*	-20	-39	-18
						299.20	-20	-38	-20
44	Benzylsildenafil	苄西地那非	1446089-82-2	8.621	551.20	377.20*	-20	-29	-18
						134.20	-20	-41	-26
45	Cinnamylsildenafil	桂地那非	1446089-83-3	9.405	555.25	117.10*	-20	-32	-12
						115.20	-20	-69	-21
46	Lodenafil carbonate	罗地那非碳酸酯	398507-55-6	17.741	518.30	487.30*	-26	-22	-30
						244.10	-29	-27	-26
47	Propoxyphenylsildenafil	丙氧苯基西地那非	877777-10-1	6.409	489.25	230.20	-12	-36	-11
						283.20*	-11	-36	-20
48	Depiperazinothiosildenafil (+)	脱哌嗪基硫代西地那非	1353018-10-6	8.302	409.10	166.30	-11	-53	-11
						167.20*	-12	-36	-17
48	Depiperazinothiosildenafil (-)	脱哌嗪基硫代西地那非	1353018-10-6	8.302	407.10	381.20	-12	-28	-19
						314.10*	14	30	20
49	Acetaminotadalafil	乙酰胺基他达拉非	1446144-71-3	7.719	433.20	378.20	14	24	17
						204.10*	-10	-66	-21

50	2-Hydroxypropylnortadalafil	2-羟丙基去甲他达拉非	1353020-85-5	9.682	434.20	135.10 312.20*	-12 -10	-22 -16	-14 -22
51	Acetylvardenafil	乙酰伐地那非	1261351-28-3	4.410	467.30	135.10 151.10*	-12 -13	-24 -46	-24 -15
52	Propoxyphenyl hydroxyhomosildenafil	丙氧苯基羟基豪莫西地那非	139755-87-6	6.443	519.20	111.20 99.20*	-10 -20	-31 -40	-20 -18
53	Propoxyphenyl thioaildenafil	丙氧苯基硫代艾地那非	856190 ⁻ 49-3	13.879	519.20	283.10 299.00*	-20 -12	-38 -37	-19 -21
54	Yohimbine	育亨宾	146-48-5	3.179	355.20	112.95 144.10*	-30 -10	-33 -30	-30 -15
55	Dapoxetine	达泊西汀	119356-77-3	6.792	306.15	212.10 157.10*	-10 -11	-24 -25	-22 -16
56	N-Desethylacetildenafil	N-去乙基红地那非	147676-55-9	4.848	439.20	127.10 99.20*	-11 -10	-50 -30	-22 -19
57	Desmethylthiosildenafil	去甲基硫代西地那非	479073-86-4	10.698	477.20	166.10 299.20*	-10 -11	-49 -37	-17 -21
58	N-Boc-N-desethyl acetildenafil	N-叔丁氧羰基-N-去乙基红地那非	1246820-46-1	9.413	539.30	327.20 439.20*	-11 -20	-29 -21	-16 -22
59	N-Ethyltadalafil	N-乙基他达拉非	1609405-34-6	10.919	404.20	99.20 135.10*	-20 -11	-37 -21	-18 -25
60	O-Desethylsildenafil	O-去乙基西地那非	139755-91-2	6.559	447.20	282.20 283.10*	-11 -10	-16 -28	-19 -19
61	Pyrazole N-desmethylsildenafil	吡唑N-去甲基西地那非	139755-95-6	3.792	461.20	299.20 100.20*	-10 -10	-31 -28	-21 -19
62	Isobutylsildenafil	异丁基西地那非	1391053-95-4	6.409	489.20	269.10 100.20*	-10 -11	-38 -29	-18 -19
63	Sildenafil dimer impurity	西地那非二聚体杂质	1346602-67-2	19.850	835.30	297.20 283.20*	-11 -20	-39 -60	-20 -19
64	Vardenafil oxopiperazine	伐地那非哌嗪酮	448184-58-5	7.932	475.15	299.10 151.10*	-20 -11	-53 -52	-21 -15
65	Sildenafil N-oxide	西地那非N-氧化物	1094598-75-0	5.732	491.20	312.20 404.20*	-11 -11	-36 -29	-22 -20
66	Vardenafil N-oxide	伐地那非N-氧化物	448184-48-3	5.370	505.20	99.20 477.25*	-20 -20	-23 -23	-24 -24
67	2-Hydroxyethylnortadalafil	2-羟乙基去甲他达拉非	385769-94-8	8.487	420.15	151.10 298.20*	-24 -12	-62 -16	-15 -21
68	Vardenafil acetyl analogue	伐地那非乙酰基类似物	/	4.377	438.25	169.10 98.20*	-12 -10	-38 -31	-17 -19
69	Vardenafil dimer (+)	伐地那非二聚体	1255919-03-9	19.342	835.30	151.10 312.20*	-10 -24	-44 -55	-15 -15
69	Vardenafil dimer (-)	伐地那非二聚体	1255919-03-9	19.345	833.30	151.20 805.20*	-24 22	-55 40	-15 22
70	Mirodenafil	米罗那非	862189-95-5	8.890	532.30	282.10 296.20*	22 -20	64 -40	18 -20
71	Mutaprodenafil	亚硝地那非	1387577-30-1	7.782	630.25	99.20 141.95*	-20 -22	-42 -29	-18 -15
72	Thioquinapiperfil	硫喹哌非	220060-39-9	5.746	449.20	312.20 204.10*	-22 -10	-42 -23	-15 -22
73	Aminosildenafil	氨基西地那非	319491-68-4	9.462	406.20	186.10 364.20*	-10 -11	-36 -24	-20 -18
74	Desethylcarbodenafil	去乙基卡巴地那非	1027192-92-2	4.165	425.25	299.20 339.20*	-11 -12	-33 -23	-21 -16
75	Didescarbonsildenafil	双去碳西地那非	466684-88-8	4.752	449.2	311.20 283.20*	-10 -10	-29 -36	-15 -19
76	N-Phenylpropenyltadalafil (+)	N-苯丙烯基他达拉非	2064212-00-4	19.275	505.20	311.20 383.10*	-12 -24	-32 -19	-22 -19
76	N-Phenylpropenyltadalafil (-)	N-苯丙烯基他达拉非	2064212-00-4	19.264	503.20	261.95 262.40*	-22 24	-32 22	-28 16
77	N-Desethyl-N-methylvardenafil	N-去乙基-N-甲基伐地那非	224785-87-9	4.964	475.20	232.30 151.10*	24 -11	45 -43	14 -15
78	Thioaildenafil	硫代艾地那非	856190-47-1	11.595	505.20	312.20 99.20*	-11 -20	-37 -34	-15 -19
						113.20	-20	-31	-21

79	Dichlorodenafil	双氯地那非	1446089-84-4	20.694	407.10	379.10*	-11	-27	-19
						350.10	-11	-32	-17
80	Piperazonifil	哌唑那非	1335201-04-1	5.667	483.20	436.30*	-11	-30	-22
						166.10	-11	-53	-17
81	Propoxyphenyl thiosildenafil	丙氧苯基硫代西地那非	479073-87-5	12.912	505.20	299.15*	-14	-38	-21
						313.20	-30	-33	-30
82	Propoxyphenyl thiohomosildenafil	丙氧苯基硫代豪莫西地那非	479073-88-6	13.019	519.20	299.10*	-20	-39	-20
						113.20	-20	-31	-20
83	Dithiodesethyl carbodenafil	二硫代去乙基卡巴地那非	1610830-81-3	11.345	457.20	371.20*	-10	-23	-18
						343.10	-10	-34	-24
84	Hydroxythioacetildenafil	羟基硫代红地那非	1159977-47-5	9.773	499.20	127.20*	-11	-31	-13
						143.20	-11	-32	-15
85	Tadalafil dichloro impurity	他达拉非二氯代杂质	1598416-08-0	15.251	461.00	134.95*	-30	-21	-14
						204.10	-30	-68	-22
86	Sildenafil impurity 12	西地那非杂质12	/	12.538	499.20	343.15*	-11	-38	-24
						371.15	-30	-27	-30
87	Demethylpiperaziny sildenafil sulfonic acid	去甲基哌嗪基西地那非磺酸	1357931-55-5	5.410	393.10	365.20*	-11	-27	-26
						256.10	-11	-34	-28
88	Propoxyphenyl aildenafil	丙氧苯基艾地那非	1391053-82-9	7.014	503.20	283.10*	-24	-38	-19
						113.25	-24	-31	-22
89	Sildenafil impurity 14	西地那非杂质14	2146091-79-2	12.741	485.20	343.10*	-11	-36	-24
						371.20	-11	-25	-18
90	Propoxyphenylisobutyl aildenafil	丙氧苯基异丁基艾地那非	1621873-33-3	8.503	517.30	297.35*	-20	-38	-20
						113.20	-20	-32	-22

*代表定量离子对。

1.3 标准溶液配制

取 90 种那非类化合物混合标准贮备液 (5 mg/L)，以纯甲醇逐级稀释为 0.1、0.2、0.5、1、2、5、10、20、50 ng/mL 的九个不同浓度的混合标准工作溶液。

1.4 样品前处理

取试样 (饮料、酒) 适量摇匀，准确吸取 1 mL 置于 50 mL 容量瓶中，加甲醇适量，超声提取 15 min，放冷至室温，用甲醇定容，经有机相微孔滤膜过滤，取滤液待测。

建议实验全过程采用塑料容器，以避免少数那非类化合物对于玻璃器皿的吸附。

结果与讨论

2.1 混合标准样品色谱图

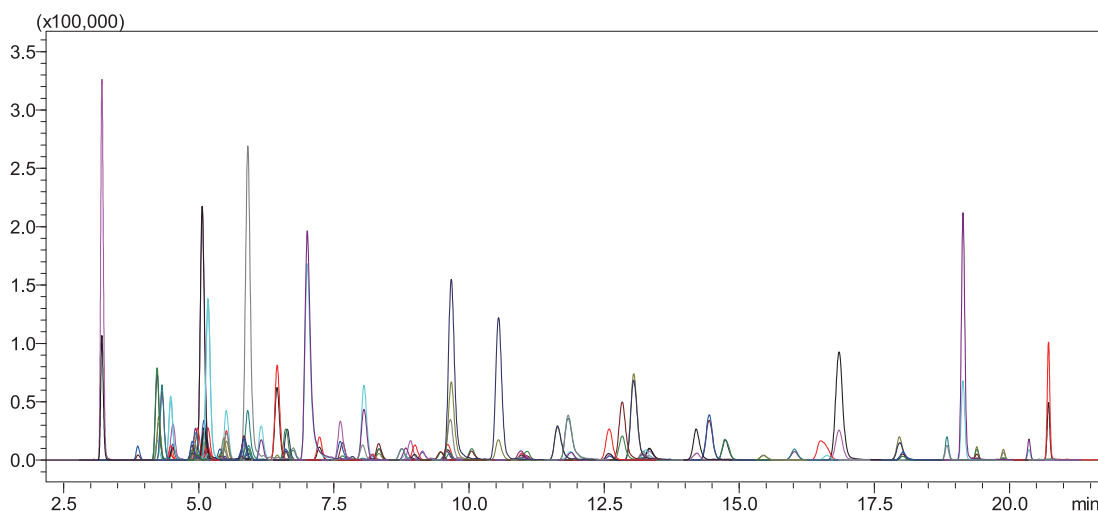


图1 90种那非类化合物标准品色谱图 (1.0 ng/mL)

2.2 线性关系

按照 1.3 配制九个不同浓度的混合标准工作溶液，按照 1.2 中的分析条件进行测定，以浓度为横坐标，峰面积为纵坐标，外标法绘制标准曲线。各化合物线性方程、线性范围、相关系数、检出限 (S/N=3, 软件计算) 和定量限 (S/N=10, 软件计算) 结果见表 3。90 种那非类化合物校准曲线在 0.1~50 ng/mL 浓度范围内，相关系数大于 0.998，线性良好。检出限在 0.0007~0.1379 ng/mL 之间，定量限在 0.0021~0.4221 ng/mL 之间，灵敏度高。

表3 线性关系、检出限和定量限 (权重1/C)

编号	化合物名称	校准曲线	线性范围 (ng/mL)	准确度(%)	相关系数r	检出限 (ng/mL)	定量限 (ng/mL)
1	Sildenafil	$Y = (52493.4)X + (-1849.75)$	0.1-50	82.9-109.8	0.9996	0.0207	0.0628
2	Tadalafil	$Y = (63354.4)X + (-2263.43)$	0.1-50	92.4-113.2	0.9998	0.0088	0.0267
3	Imidazosagatriazinone	$Y = (1.01399e+006)X + (-11262.0)$	0.1-50	96.8-108.4	0.9999	0.0032	0.0098
4	Gildenafil	$Y = (348548)X + (-2738.93)$	0.1-50	92.5-109.3	0.9998	0.0059	0.0180
5	Acetil acid	$Y = (227101)X + (-3825.70)$	0.1-50	88.8-110.0	0.9998	0.0144	0.0435
6	Xanthoanthrafil	$Y = (93334.8)X + (-2119.44)$	0.1-50	90.5-107.6	0.9998	0.0076	0.0229
7	Aminotadalafil	$Y = (235077)X + (-3694.59)$	0.1-50	87.3-108.5	0.9999	0.0066	0.0200
8	Chloropretadalafil	$Y = (40806.1)X + (-669.973)$	0.1-50	89.5-106.5	0.9995	0.0328	0.0995
9	Piperiacetildenafil	$Y = (842203)X + (-4958.30)$	0.1-20	96.2-105.9	0.9999	0.0049	0.0148
10	Noracetildenafil	$Y = (152262)X + (-620.495)$	0.1-20	87.1-109.5	0.9993	0.0161	0.0488
11	Carbodenafil	$Y = (334896)X + (-2276.67)$	0.1-50	90.0-113.6	0.9998	0.0060	0.0183
12	Pseudovardenafil	$Y = (861629)X + (-99.7632)$	0.1-50	92.8-106.7	0.9996	0.0008	0.0024
13	Norneosildenafil	$Y = (95930.2)X + (-633.023)$	0.1-50	89.9-105.9	0.9996	0.0132	0.0401
14	N-Desethylvaridenafil	$Y = (86785.7)X + (1528.99)$	0.1-20	85.3-110.9	0.9997	0.0049	0.0148
15	N-Desmethylsildenafil	$Y = (98577.1)X + (-1760.82)$	0.1-50	89.7-109.7	0.9995	0.0126	0.0382
16	Acetildenafil	$Y = (197616)X + (887.250)$	0.1-20	89.5-110.0	0.9991	0.0050	0.0153
17	Hydroxyacetildenafil	$Y = (49433.2)X + (-65.0266)$	0.1-20	85.0-111.5	0.9996	0.0147	0.0445
18	Avanafil	$Y = (1.23387e+006)X + (13335.7)$	0.1-20	90.1-107.4	0.9994	0.0022	0.0068
19	Aildenafil	$Y = (91944.7)X + (1320.76)$	0.1-50	86.6-113.1	0.9992	0.0131	0.0397
20	Homosildenafil	$Y = (20029.8)X + (-2839.67)$	0.2-20	92.8-113.9	0.9995	0.0238	0.0722
21	Vardenafil	$Y = (105430)X + (577.532)$	0.1-20	85.0-112.7	0.9994	0.0025	0.0077
22	Thiosildenafil	$Y = (20311.4)X + (-3183.29)$	0.5-50	87.0-112.4	0.9998	0.0405	0.1227
23	Thiohomosildenafil	$Y = (39308.2)X + (-6266.29)$	0.5-50	88.5-108.5	0.9998	0.0322	0.0977
24	Hydroxyvaridenafil	$Y = (62739.9)X + (1533.29)$	0.1-20	85.9-113.5	0.9995	0.0131	0.0396
25	Hydroxyhomosildenafil	$Y = (40423.7)X + (-8870.15)$	0.5-20	85.6-110.5	0.9991	0.0770	0.2334
26	Udenafil	$Y = (528133)X + (2836.63)$	0.1-20	88.1-111.3	0.9996	0.0009	0.0026
27	Hydroxythiohomosildenafil	$Y = (74446.4)X + (-6209.99)$	0.2-50	91.6-109.6	0.9998	0.0238	0.0722
28	Norneovardenafil	$Y = (993184)X + (-27170.0)$	0.1-50	90.7-109.4	0.9998	0.0053	0.0161
29	Nitrodenafil	$Y = (158670)X + (-3362.71)$	0.1-50	91.5-112.1	0.9998	0.0122	0.0369
30	Nortadalafil	$Y = (38809.0)X + (37.1953)$	0.2-50	92.4-108	0.9996	0.0231	0.0699

31	Chlorodenafil	$Y = (79681.8)X + (-1128.66)$	0.1-50	90.1-103.1	0.9998	0.0143	0.0434
32	Hydroxychlorodenafil	$Y = (164818)X + (-59.2093)$	0.1-50	94.2-105.8	0.9997	0.0264	0.0801
33	N-Butyltadalafil	$Y = (37413.0)X + (-1255.79)$	0.2-50	94.7-103.9	0.9999	0.0113	0.0343
34	Desmethylcarbodenafil	$Y = (388004)X + (2270.05)$	0.1-50	87.8-105.1	0.9996	0.0024	0.0074
35	Descarbonsildenafil	$Y = (85082.8)X + (522.866)$	0.1-20	88.8-112.6	0.9996	0.0036	0.0110
36	Dimethylacetildenafil	$Y = (127961)X + (953.809)$	0.1-20	87.8-111.3	0.9991	0.0138	0.0418
37	Dithio-desmethylcarbodenafil	$Y = (512590)X + (-145462)$	0.5-50	89.0-115.0	0.9996	0.0176	0.0533
38	Oxohongdenafil	$Y = (65329.1)X + (-1740.26)$	0.1-50	92.6-105.6	0.9995	0.0009	0.0027
39	N-Octylnortadalafil	$Y = (64924.4)X + (1126.80)$	0.1-50	86.2-105.3	0.9992	0.0077	0.0234
40	Dioxohongdenafil	$Y = (113647)X + (1284.53)$	0.1-50	92.7-108.9	0.9998	0.0014	0.0043
41	Hydroxythiovarndenafil	$Y = (90382.9)X + (8.49455)$	0.1-50	91.2-108.6	0.9990	0.0098	0.0298
42	Cyclopentynafil Propoxyphenyl	$Y = (165184)X + (1656.54)$	0.1-50	90.7-108.5	0.9992	0.0019	0.0059
43	Thiohydroxyhomo sildenafil	$Y = (81082.8)X + (-3678.87)$	0.1-50	90.7-112.8	0.9998	0.0211	0.0640
44	Benzylsildenafil	$Y = (77687.4)X + (-1720.34)$	0.1-50	90.2-108.2	0.9997	0.0097	0.0295
45	Cinnamylndenafil	$Y = (1.29594e+006)X + (-22984.9)$	0.1-20	94.7-104.1	0.9997	0.0010	0.0029
46	Lodenafil carbonate	$Y = (58665.9)X + (-8754.62)$	0.5-50	91.7-111.7	0.9991	0.0410	0.1241
47	Propoxyphenylsildenafil	$Y = (63497.6)X + (68.9150)$	0.2-50	88.2-109.5	0.9996	0.0313	0.0947
48	Depiperazinothio sildenafil (+)	$Y = (97972.8)X + (-1163.38)$	0.1-50	87.5-111.6	0.9999	0.0105	0.0319
48	Depiperazinothio sildenafil (-)	$Y = (64879.5)X + (-276.580)$	0.1-50	88.7-112.5	0.9998	0.0060	0.0181
49	Acetaminotadalafil	$Y = (20152.2)X + (400.171)$	0.5-50	90.1-107.2	0.9998	0.0188	0.0570
50	2-Hydroxypropylnortadalafil	$Y = (18259.0)X + (-963.744)$	0.5-50	92.7-108.4	0.9995	0.1253	0.3797
51	Acetylvarndenafil Propoxyphenyl	$Y = (186432)X + (-78.8775)$	0.1-20	86.6-110.6	0.9990	0.0074	0.0224
52	hydroxyhomosildenafil Propoxyphenyl	$Y = (167381)X + (-879.791)$	0.1-50	85.1-106.7	0.9997	0.0035	0.0105
53	thioailndenafil	$Y = (273194)X + (-6894.47)$	0.1-50	90.1-111.8	0.9997	0.0255	0.0772
54	Yohimbine	$Y = (1.15926e+006)X + (-5036.05)$	0.1-20	95.8-104.2	0.9999	0.0007	0.0021
55	Dapoxetine	$Y = (1.53509e+006)X + (-21148.3)$	0.1-50	96.8-104.4	0.9998	0.0015	0.0045
56	N-Desethylacetildenafil	$Y = (154854)X + (2095.35)$	0.1-20	89.1-109.6	0.9990	0.0260	0.0788
57	Desmethylthiosildenafil N-Boc-N-desethyl	$Y = (55162.0)X + (-9275.39)$	0.5-50	85.5-113.3	0.9996	0.0416	0.1261
58	acetildenafil	$Y = (273657)X + (-4039.75)$	0.1-50	93.6-105.0	0.9998	0.0033	0.0100
59	N-Ethyltadalafil	$Y = (61388.1)X + (-1524.63)$	0.1-50	92.1-108.7	0.9999	0.0111	0.0335
60	O-Desethylsildenafil Pyrazole	$Y = (77566.7)X + (-852.783)$	0.1-50	89.4-109.6	0.9998	0.0277	0.0839
61	N-desmethylsildenafil	$Y = (54765.7)X + (794.412)$	0.1-50	92.3-110.6	0.9995	0.0081	0.0245
62	Isobutylsildenafil	$Y = (173672)X + (-725.553)$	0.1-50	90.8-104.7	0.9997	0.0024	0.0073
63	Sildenafil dimer impurity	$Y = (20747.7)X + (496.758)$	0.2-20	86.0-107.5	0.9999	0.0176	0.0532
64	Vardenafil oxopiperazine	$Y = (455943)X + (4873.99)$	0.1-50	94.6-105.0	0.9999	0.0033	0.0101
65	Sildenafil N-oxide	$Y = (80788.0)X + (859.040)$	0.1-50	94.3-109.1	0.9994	0.0106	0.0320

66	Vardenafil N-oxide	$Y = (243660)X + (1336.92)$	0.1-50	86.3-106.3	0.9991	0.0070	0.0212
67	2-Hydroxyethylnor tadalafil	$Y = (31792.0)X + (-457.678)$	0.2-50	91.0-111.4	0.9996	0.0298	0.0903
68	Vardenafil acetyl analogue	$Y = (268684)X + (-111.528)$	0.1-20	87.5-108.2	0.9993	0.0020	0.0059
69	Vardenafil dimer (+)	$Y = (45497.8)X + (-1506.98)$	0.1-50	89.6-107.5	0.9992	0.0264	0.0800
69	Vardenafil dimer (-)	$Y = (53305.5)X + (-483.201)$	0.1-50	92.0-110.6	0.9999	0.0072	0.0219
70	Mirodenafil	$Y = (57104.2)X + (-1120.21)$	0.1-50	91.1-108.0	0.9996	0.0071	0.0216
71	Mutaprodenafil	$Y = (88084.3)X + (-614.563)$	0.1-50	90.7-108.8	0.9990	0.0121	0.0366
72	Thioquinapiperfil	$Y = (1.89825e+006)X + (-68472.7)$	0.1-50	91.8-106.9	0.9989	0.0041	0.0125
73	Aminosildenafil	$Y = (104905)X + (-2121.30)$	0.1-50	92.8-104.7	0.9998	0.0140	0.0425
74	Desethylcarbodenafil	$Y = (178444)X + (-805.307)$	0.1-50	88.0-112.6	0.9997	0.0055	0.0166
75	Didescarbongsildenafil	$Y = (97259.6)X + (-2467.70)$	0.1-50	89.1-108.6	0.9996	0.0080	0.0244
76	N-Phenylpropenyl tadalafil (+)	$Y = (11703.5)X + (-287.958)$	0.5-50	87.5-107.5	0.9997	0.1393	0.4221
76	N-Phenylpropenyl tadalafil (-)	$Y = (4847.98)X + (57.8305)$	0.5-50	88.6-108.6	0.9995	0.1379	0.4180
77	N-Desethyl-N-methyl var denafil	$Y = (118175)X + (244.781)$	0.1-20	87.2-111.5	0.9994	0.0049	0.0149
78	Thioaildenafil	$Y = (69533.2)X + (3367.93)$	0.2-50	89.2-111.7	0.9997	0.0389	0.1178
79	Dichlorodenafil	$Y = (314294)X + (10414.1)$	0.1-50	85.5-106.6	0.9997	0.0069	0.0209
80	Piperazonifil	$Y = (50539.4)X + (-712.163)$	0.2-50	86.6-109.6	0.9994	0.0422	0.1278
81	Propoxyphenyl thiosildenafil	$Y = (81550.7)X + (-12405.6)$	0.5-50	90.1-108.4	0.9997	0.0221	0.0669
82	Propoxyphenyl thiohomosildenafil	$Y = (98169.5)X + (-8631.39)$	0.2-50	87.7-113.6	0.9998	0.0605	0.1834
83	Dithiodesethyl carbodenafil	$Y = (349865)X + (-89360.1)$	0.5-50	90.6-115.9	0.9996	0.0255	0.0774
84	Hydroxythioacetildenafil	$Y = (89554.1)X + (-6779.36)$	0.2-50	91.8-107.3	0.9994	0.0161	0.0487
85	Tadalafil dichloro impurity	$Y = (41168.4)X + (-2174.28)$	0.2-50	88.9-115.4	0.9998	0.0287	0.0871
86	Sildenafil impurity 12	$Y = (570727)X + (-112257)$	0.5-50	91.9-112.4	0.9997	0.0099	0.0301
87	Demethylpiperaziny sildenafil sulfonic acid	$Y = (18105.8)X + (-2088.66)$	0.5-50	88.7-110.8	0.9998	0.0611	0.1850
88	Propoxyphenyl aildenafil	$Y = (116590)X + (-48.6511)$	0.1-50	89.1-111.9	0.9995	0.0179	0.0544
89	Sildenafil impurity 14	$Y = (813346)X + (-167325)$	0.5-50	90.2-114.6	0.9997	0.0020	0.0060
90	Propoxyphenylisobutyl aildenafil	$Y = (79158.4)X + (-1467.57)$	0.1-50	90.3-109.8	0.9996	0.0046	0.0140

2.1 精密度实验

对 2 ng/mL 的混合标准溶液连续 6 次进样，考察仪器的精密度，保留时间和峰面积的重复性结果如表 4 所示。保留时间和峰面积的相对标准偏差分别在 0.02~0.34% 和 1.22~4.96% 之间，仪器精密度良好。

表4 保留时间和峰面积重复性结果(n=6)

No.	名称	RSD%		No.	名称	RSD%	
		R.T.	Area			R.T.	Area
1	Sildenafil	0.19	4.90	148	Depiperazinothiosildenafil (+)	0.20	2.68
2	Tadalafil	0.22	3.97	48	Depiperazinothiosildenafil (-)	0.20	4.69
3	Imidazosagatriazinone	0.04	2.03	49	Acetaminotadalafil	0.25	4.26
4	Gendenafil	0.16	1.55	50	2-Hydroxypropylnortadalafil	0.24	4.89
5	Acetil acid	0.19	2.47	51	Acetylvardenafil	0.16	3.00
6	Xanthoanthrafil	0.24	2.36	52	Propoxyphenyl hydroxyhomosildenafil	0.33	2.15
7	Aminotadalafil	0.23	1.75	53	Propoxyphenyl thioaildenafil	0.18	1.22
8	Chloropretadalafil	0.17	2.97	54	Yohimbine	0.21	2.14
9	Piperiacetildenafil	0.17	2.59	55	Dapoxetine	0.29	2.57
10	Noracetildenafil	0.14	3.83	56	N-Desethylacetildenafil	0.16	3.57
11	Carbodenafil	0.14	1.90	57	Desmethylthiosildenafil	0.26	3.93
12	Pseudovardenafil	0.13	2.16	58	N-Boc-N-desethyl acetildenafil	0.27	3.25
13	Norneosildenafil	0.05	3.37	59	N-Ethyltadalafil	0.20	4.91
14	N-Desethylvardenafil	0.20	4.53	60	O-Desethylsildenafil	0.29	4.14
15	N-Desmethylsildenafil	0.18	3.91	61	Pyrazole N-desmethylsildenafil	0.18	4.76
16	Acetildenafil	0.18	2.56	62	Isobutylsildenafil	0.30	2.43
17	Hydroxyacetildenafil	0.18	4.36	63	Sildenafil dimer impurity	0.02	4.08
18	Avanafil	0.16	1.80	64	Vardenafil oxopiperazine	0.22	2.72
19	Aildenafil	0.27	3.64	65	Sildenafil N-oxide	0.26	4.50
20	Homosildenafil	0.22	4.13	66	Vardenafil N-oxide	0.20	4.26
21	Vardenafil	0.18	4.71	67	2-Hydroxyethylnortadalafil	0.27	4.94
22	Thiosildenafil	0.32	4.17	68	Vardenafil acetyl analogue	0.13	1.50
23	Thiohomosildenafil	0.25	4.68	69	Vardenafil dimer (+)	0.03	3.79
24	Hydroxyvardenafil	0.18	3.90	69	Vardenafil dimer (-)	0.03	2.76
25	Hydroxyhomosildenafil	0.21	3.93	70	Mirodenafil	0.30	4.94
26	Udenafil	0.31	3.15	71	Mutaprodenafil	0.33	2.53
27	Hydroxythiohomosildenafil	0.24	2.90	72	Thioquinapiperfil	0.22	1.47
28	Norneovardenafil	0.20	2.09	73	Aminosildenafil	0.23	4.03
29	Nitrodenafil	0.10	2.44	74	Desethylcarbodenafil	0.16	4.05
30	Nortadalafil	0.21	4.70	75	Didescarbongsildenafil	0.13	3.14
31	Chlorodenafil	0.14	2.41	76	N-Phenylpropenyltadalafil (+)	0.03	4.18
32	Hydroxychlorodenafil	0.16	2.28	76	N-Phenylpropenyltadalafil (-)	0.04	4.41
33	N-Butyltadalafil	0.14	2.52	77	N-Desethyl-N-methylvardenafil	0.21	4.34
34	Desmethylcarbodenafil	0.15	3.24	78	Thioaildenafil	0.21	2.90
35	Descarbongsildenafil	0.18	4.63	79	Dichlorodenafil	0.02	2.69
36	Dimethylacetildenafil	0.23	2.28	80	Piperazonifil	0.21	4.42
37	Dithio-desmethylcarbodenafil	0.22	3.03	81	Propoxyphenyl thiosildenafil	0.18	4.96
38	Oxohongdenafil	0.22	3.55	82	Propoxyphenyl thiohomosildenafil	0.20	3.48
39	N-Octylnortadalafil	0.02	2.46	83	Dithiodesethyl carbodenafil	0.24	1.61
40	Dioxohongdenafil	0.24	3.18	84	Hydroxythioacetildenafil	0.26	2.32
41	Hydroxythiovardenafil	0.26	3.06	85	Tadalafil dichloro impurity	0.14	2.65
42	Cyclopentynafil	0.27	4.22	86	Sildenafil impurity 12	0.21	1.58
43	Propoxyphenyl thiohydroxyhomosildenafil	0.21	2.66	87	Demethylpiperaziny sildenafil sulfonic acid	0.13	4.96
44	Benzylsildenafil	0.23	4.33	88	Propoxyphenyl aildenafil	0.34	4.57
45	Cinnamylildenafil	0.30	2.03	89	Sildenafil impurity 14	0.20	0.99
46	Lodenafil carbonate	0.09	3.66	90	Propoxyphenylisobutyl aildenafil	0.26	3.05
47	Propoxyphenylsildenafil	0.33	2.32				

2.4 加标回收实验

取 1 mL 样品，加入那非类化合物混合标准溶液，配制成浓度为 100 ng/mL 的加标样品，按照 1.4 中的方法进行前处理，上机分析。抗疲劳饮料样品色谱图和补肾药酒样品色谱图见图 2~ 图 3。加标回收结果见表 5。该抗疲劳样品中检出 Sildenafil，浓度为 38.85 ng/mL。抗疲劳饮料样品有 89 种化合物加标回收率在 81.6~113.5% 之间。药酒样品有 82 种化合物加标回收率在 80.2~111.9% 之间，有 4 种化合物加标回收率在 70.6~79.9% 之间。

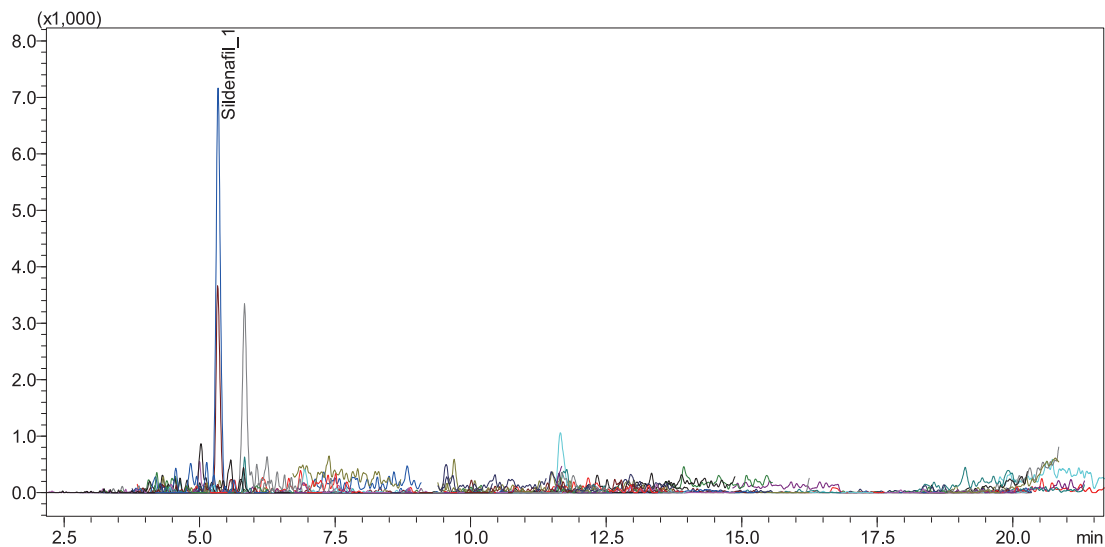


图2 抗疲劳饮料样品

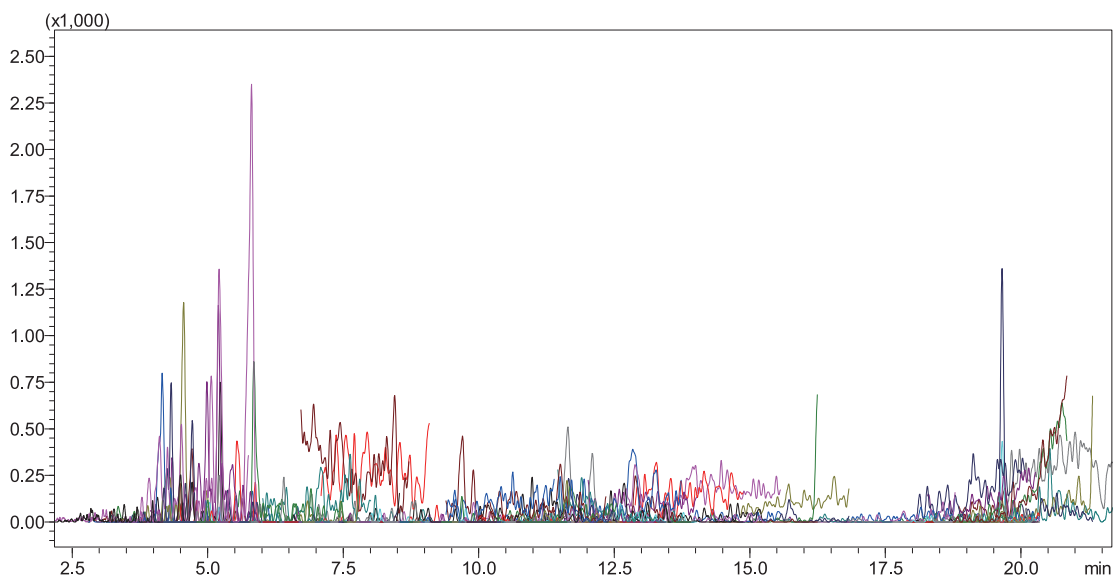


图3 补肾药酒样品

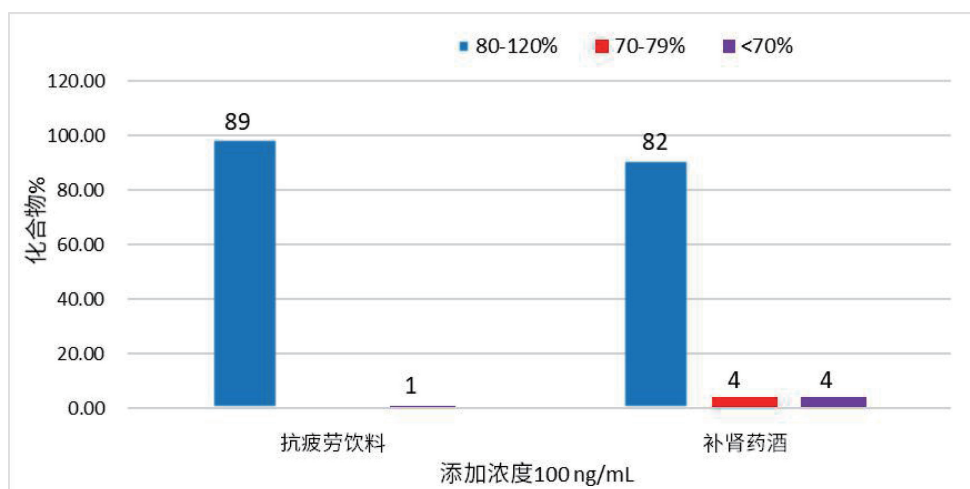


图4 抗疲劳饮料和补肾药酒回收率统计

表5 样品加标回收率 (加标浓度100 ng/mL)

抗疲劳饮料				补肾药酒			
No.	名称	样品浓度 ng/mL	加标回 收率%	No.	名称	样品浓度 ng/mL	加标回 收率%
1	Sildenafil	38.85	109.9	1	Sildenafil	N.D.	102.3
2	Tadalafil	N.D.	103.6	2	Tadalafil	N.D.	108.1
3	Imidazosagatriazinone	N.D.	100.3	3	Imidazosagatriazinone	N.D.	100.5
4	Gildenafil	N.D.	100.3	4	Gildenafil	N.D.	102.5
5	Acetil acid	N.D.	104.1	5	Acetil acid	N.D.	102.7
6	Xanthoanthrafil	N.D.	109.2	6	Xanthoanthrafil	N.D.	111.1
7	Aminotadalafil	N.D.	106.3	7	Aminotadalafil	N.D.	108.8
8	Chloropretadalafil	N.D.	99.7	8	Chloropretadalafil	N.D.	97.3
9	Piperiacetildenafil	N.D.	93.8	9	Piperiacetildenafil	N.D.	80.2
10	Noracetildenafil	N.D.	88.5	10	Noracetildenafil	N.D.	77.0
11	Carbodenafil	N.D.	101.8	11	Carbodenafil	N.D.	101.1
12	Pseudovardenafil	N.D.	100.8	12	Pseudovardenafil	N.D.	99.4
13	Norneosildenafil	N.D.	99.1	13	Norneosildenafil	N.D.	102.1
14	N-Desethylvaridenafil	N.D.	92.9	14	N-Desethylvaridenafil	N.D.	96.3
15	N-Desmethylsildenafil	N.D.	106.5	15	N-Desmethylsildenafil	N.D.	111.9
16	Acetildenafil	N.D.	91.9	16	Acetildenafil	N.D.	79.9
17	Hydroxyacetildenafil	N.D.	96.7	17	Hydroxyacetildenafil	N.D.	82.8
18	Avanafil	N.D.	91.9	18	Avanafil	N.D.	89.8
19	Aildenafil	N.D.	102.8	19	Aildenafil	N.D.	99.6
20	Homosildenafil	N.D.	111.0	20	Homosildenafil	N.D.	106.1
21	Vardenafil	N.D.	84.3	21	Vardenafil	N.D.	89.5
22	Thiosildenafil	N.D.	104.7	22	Thiosildenafil	N.D.	103.9
23	Thiohomosildenafil	N.D.	97.7	23	Thiohomosildenafil	N.D.	95.1
24	Hydroxyvaridenafil	N.D.	91.8	24	Hydroxyvaridenafil	N.D.	101.8
25	Hydroxyhomosildenafil	N.D.	96.4	25	Hydroxyhomosildenafil	N.D.	96.2
26	Udenafil	N.D.	95.9	26	Udenafil	N.D.	70.6
27	Hydroxythiohomosildenafil	N.D.	97.8	27	Hydroxythiohomosildenafil	N.D.	98.2
28	Norneovardenafil	N.D.	102.4	28	Norneovardenafil	N.D.	101.4
29	Nitrodenafil	N.D.	100.2	29	Nitrodenafil	N.D.	101.3
30	Nortadalafil	N.D.	109.2	30	Nortadalafil	N.D.	104.0
31	Chlorodenafil	N.D.	102.8	31	Chlorodenafil	N.D.	102.8
32	Hydroxychlorodenafil	N.D.	102.3	32	Hydroxychlorodenafil	N.D.	103.8
33	N-Butyltadalafil	N.D.	105.0	33	N-Butyltadalafil	N.D.	105.5
34	Desmethylcarbodenafil	N.D.	105.4	34	Desmethylcarbodenafil	N.D.	106.5
35	Descarbonsildenafil	N.D.	101.3	35	Descarbonsildenafil	N.D.	89.5

36	Dimethylacetildenafil	N.D.	89.1	36	Dimethylacetildenafil	N.D.	41.0
37	Dithio-desmethylcarbodenafil	N.D.	98.0	37	Dithio-desmethylcarbodenafil	N.D.	93.8
38	Oxohongdenafil	N.D.	99.5	38	Oxohongdenafil	N.D.	97.7
39	N-Octylnortadalafil	N.D.	107.4	39	N-Octylnortadalafil	N.D.	104.6
40	Dioxohongdenafil	N.D.	101.8	40	Dioxohongdenafil	N.D.	106.0
41	Hydroxythiovardenafil	N.D.	101.2	41	Hydroxythiovardenafil	N.D.	100.4
42	Cyclopentynafil	N.D.	96.5	42	Cyclopentynafil	N.D.	96.3
43	Propoxyphenyl thiohydroxyhomosildenafil	N.D.	96.3	43	Propoxyphenyl thiohydroxyhomosildenafil	N.D.	97.0
44	Benzylsildenafil	N.D.	108.5	44	Benzylsildenafil	N.D.	109.5
45	Cinnamylidenafil	N.D.	100.3	45	Cinnamylidenafil	N.D.	93.9
46	Lodenafil carbonate	N.D.	99.9	46	Lodenafil carbonate	N.D.	102.5
47	Propoxyphenylsildenafil	N.D.	108.1	47	Propoxyphenylsildenafil	N.D.	96.8
48	Depiperazinothiosildenafil (+)	N.D.	102.0	48	Depiperazinothiosildenafil (+)	N.D.	105.8
48	Depiperazinothiosildenafil (-)	N.D.	101.5	48	Depiperazinothiosildenafil (-)	N.D.	101.3
49	Acetaminotadalafil	N.D.	94.1	49	Acetaminotadalafil	N.D.	108.2
50	2-Hydroxypropylnortadalafil	N.D.	108.2	50	2-Hydroxypropylnortadalafil	N.D.	112.0
51	Acetylvardenafil	N.D.	81.6	51	Acetylvardenafil	N.D.	65.7
52	Propoxyphenyl hydroxyhomosildenafil	N.D.	102.2	52	Propoxyphenyl hydroxyhomosildenafil	N.D.	102.7
53	Propoxyphenyl thioaildenafil	N.D.	101.8	53	Propoxyphenyl thioaildenafil	N.D.	102.1
54	Yohimbine	N.D.	67.8	54	Yohimbine	N.D.	72.5
55	Dapoxetine	N.D.	102.6	55	Dapoxetine	N.D.	102.8
56	N-Desethylacetildenafil	N.D.	83.6	56	N-Desethylacetildenafil	N.D.	68.6
57	Desmethylthiosildenafil	N.D.	104.7	57	Desmethylthiosildenafil	N.D.	100.1
58	N-Boc-N-desethyl acetildenafil	N.D.	99.6	58	N-Boc-N-desethyl acetildenafil	N.D.	94.1
59	N-Ethyltadalafil	N.D.	105.3	59	N-Ethyltadalafil	N.D.	101.2
60	O-Desethylsildenafil	N.D.	104.0	60	O-Desethylsildenafil	N.D.	106.2
61	Pyrazole N-desmethylsildenafil	N.D.	105.5	61	Pyrazole N-desmethylsildenafil	N.D.	102.1
62	Isobutylsildenafil	N.D.	105.0	62	Isobutylsildenafil	N.D.	104.2
63	Sildenafil dimer impurity	N.D.	103.3	63	Sildenafil dimer impurity	N.D.	98.4
64	Vardenafil oxopiperazine	N.D.	100.6	64	Vardenafil oxopiperazine	N.D.	101.5
65	Sildenafil N-oxide	N.D.	100.2	65	Sildenafil N-oxide	N.D.	91.6
66	Vardenafil N-oxide	N.D.	98.5	66	Vardenafil N-oxide	N.D.	95.5
67	2-Hydroxyethylnortadalafil	N.D.	112.5	67	2-Hydroxyethylnortadalafil	N.D.	112.4
68	Vardenafil acetyl analogue	N.D.	88.8	68	Vardenafil acetyl analogue	N.D.	74.0
69	Vardenafil dimer (+)	N.D.	97.2	69	Vardenafil dimer (+)	N.D.	95.8
69	Vardenafil dimer (-)	N.D.	99.8	69	Vardenafil dimer (-)	N.D.	102.5
70	Mirodenafil	N.D.	103.5	70	Mirodenafil	N.D.	91.9
71	Mutaprodenafil	N.D.	101.6	71	Mutaprodenafil	N.D.	97.5
72	Thioquinapiperfil	N.D.	95.7	72	Thioquinapiperfil	N.D.	46.3
73	Aminosildenafil	N.D.	99.8	73	Aminosildenafil	N.D.	97.5
74	Desethylcarbodenafil	N.D.	103.0	74	Desethylcarbodenafil	N.D.	100.7
75	Didescarbonsildenafil	N.D.	113.5	75	Didescarbonsildenafil	N.D.	110.8
76	N-Phenylpropenyltadalafil (+)	N.D.	98.8	76	N-Phenylpropenyltadalafil (+)	N.D.	96.6
76	N-Phenylpropenyltadalafil (-)	N.D.	95.1	76	N-Phenylpropenyltadalafil (-)	N.D.	107.4
77	N-Desethyl-N-methylvardenafil	N.D.	90.6	77	N-Desethyl-N-methylvardenafil	N.D.	97.8
78	Thioaildenafil	N.D.	99.6	78	Thioaildenafil	N.D.	98.6
79	Dichlorodenafil	N.D.	98.8	79	Dichlorodenafil	N.D.	100.6
80	Piperazonifil	N.D.	108.8	80	Piperazonifil	N.D.	105.9
81	Propoxyphenyl thiosildenafil	N.D.	98.2	81	Propoxyphenyl thiosildenafil	N.D.	102.8
82	Propoxyphenyl thiohomosildenafil	N.D.	100.6	82	Propoxyphenyl thiohomosildenafil	N.D.	105.2
83	Dithiodesethyl carbodenafil	N.D.	100.8	83	Dithiodesethyl carbodenafil	N.D.	99.4
84	Hydroxythioacetildenafil	N.D.	96.0	84	Hydroxythioacetildenafil	N.D.	85.9
85	Tadalafil dichloro impurity	N.D.	106.2	85	Tadalafil dichloro impurity	N.D.	105.8
86	Sildenafil impurity 12	N.D.	101.6	86	Sildenafil impurity 12	N.D.	100.8
87	Demethylpiperaziny sildenafil sulfonic acid	N.D.	112.2	87	Demethylpiperaziny sildenafil sulfonic acid	N.D.	108.3
88	Propoxyphenyl aildenafil	N.D.	101.2	88	Propoxyphenyl aildenafil	N.D.	99.6
89	Sildenafil impurity 14	N.D.	99.2	89	Sildenafil impurity 14	N.D.	99.8
90	Propoxyphenylisobutyl aildenafil	N.D.	103.5	90	Propoxyphenylisobutyl aildenafil	N.D.	96.3

2.5 实际样品分析

使用本方法分析了三种品牌的抗疲劳饮料，每个样品平行分析两次，品牌 1 和品牌 2 检出西地那非，未检出其他化合物。品牌 3 未检出任何化合物。西地那非定量结果见表 6。

表6 样品分析结果

样品名称	分析结果
品牌1	西地那非 (Sildenafil) ,38.85 ng/mL
品牌2	西地那非 (Sildenafil) ,51.15 ng/mL
品牌3	未检出

结论

本文建立了一种使用岛津超高效液相色谱仪 LC-30A 和三重四极杆质谱仪 LCMS-8050 联用测定抗疲劳饮料和补肾药酒中 90 种那非类化合物的方法。本方法基于国家市场监督管理总局发布的标准，可在 25 min 内正负离子同时检测 90 种那非类化合物。方法线性范围宽、重复性好、准确度高，优于食品补充检验方法标准要求。使用本方法测定了三个品牌的抗疲劳饮料样品，其中两个品牌检出西地那非 (Sildenafil)。补肾药酒中未检出 90 种那非类化合物。本方法简单、快速、灵敏、准确，可用于食品中 90 种那非类物质的定量检测和定性筛查。