

# SN

## 中华人民共和国出入境检验检疫行业标准

SN/T 4062—2014

### 出口植物性中药材中稀土 元素的测定方法

Determination of rare earth elements in botanic  
Chinese medicinal material for export

2014-11-19 发布

2015-05-01 实施



中 华 人 民 共 和 国  
国家质量监督检验检疫总局 发 布

## 前 言

本标准按照 GB/T 1.1—2009 给出的规则起草。

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

本标准由国家认证认可监督管理委员会提出并归口。

本标准起草单位：中华人民共和国重庆出入境检验检疫局。

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# 出口植物性中药材中稀土 元素的测定方法

## 1 范围

本标准规定了出口植物性中药材中钪(Sc)、钇(Y)、镧(La)、铈(Ce)、镨(Pr)、钕(Nd)、钐(Sm)、铕(Eu)、钆(Gd)、铽(Tb)、镝(Dy)、钬(Ho)、铒(Er)、铥(Tm)、镱(Yb)、镱(Lu)等十六种元素(以下简称16种元素)含量的电感耦合等离子体质谱(ICP-MS)和电感耦合等离子体发射光谱(ICP-AES)测定方法。

本标准适用于人参、紫苏叶、金银花、枸杞、麻黄、黄柏等植物性中药材中16种稀土元素含量的测定。

## 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 602 化学试剂 杂质测定用标准溶液的制备

GB/T 6682 分析实验室用水规格和试验方法

## 第一法 电感耦合等离子体质谱法(ICP-MS)

## 3 原理

用硝酸-双氧水作为消解液,将试样经过微波消解后转移定容,制得样品溶液。采用电感耦合等离子体质谱仪(ICP-MS)检测样品溶液中16种元素的含量,进而计算出试样中16种元素的含量,计算其总量。

## 4 试剂

除另有规定外,所用试剂均为优级纯,水为GB/T 6682规定的一级水。

4.1 硝酸。

4.2 30%过氧化氢。

4.3 消解液:取2份硝酸(4.1)和1份过氧化氢(4.2),混匀后冷却。

4.4 硝酸溶液(1%,体积分数):取10 mL硝酸(4.1),用水稀释至1 000 mL。

4.5 16种元素标准溶液:Sc标准溶液浓度为1 000 mg/L(4.5.1),Y、La、Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm、Yb、Lu(以下简称其他15种稀土元素)混合标液浓度为100 mg/L(4.5.2)。可按GB/T 602方法配制,或者直接使用有证标准物质。

4.6 内标元素铟(In)标准溶液:浓度为1 000 mg/L。按GB/T 602方法配制,或者直接使用有证标准物质。

4.7 16种元素标准储备溶液:准确移取2.0 mL Sc标准溶液(4.5.1),及10 mL混合标液(4.5.2)于100 mL

的容量瓶中,用硝酸溶液(4.4)定容,混匀。此溶液含 Sc 20 mg/L,含其他 15 种稀土元素 10 mg/L。

4.8 内标元素 In 标准储备溶液:准确移取 1.0 mL 内标元素标准溶液(4.6),于 100 mL 的容量瓶中,用硝酸溶液(4.4)定容,混匀。此溶液含 In 10 mg/L。

4.9 16 种元素标准中间溶液:准确移取 5.0 mL 标准储备溶液(4.7),于 100 mL 的容量瓶中,用硝酸溶液(4.4)定容,混匀。此溶液含 Sc 1 000  $\mu\text{g/L}$ ,含其他 15 种稀土元素 500  $\mu\text{g/L}$ 。

4.10 16 种元素标准工作溶液:分别移取 0 mL、0.50 mL、1.0 mL、2.0 mL、5.0 mL、10.0 mL 标准中间溶液(4.9),于 100 mL 的容量瓶中,用硝酸溶液(4.4)定容,混匀。此标准工作溶液中含 Sc 浓度分别为 0  $\mu\text{g/L}$ 、5  $\mu\text{g/L}$ 、10  $\mu\text{g/L}$ 、20  $\mu\text{g/L}$ 、50  $\mu\text{g/L}$ 、100  $\mu\text{g/L}$ 。含其他 15 种稀土元素浓度分别为 0  $\mu\text{g/L}$ 、2.5  $\mu\text{g/L}$ 、5  $\mu\text{g/L}$ 、10  $\mu\text{g/L}$ 、25  $\mu\text{g/L}$ 、50  $\mu\text{g/L}$ 。该标准工作溶液均为用时现配。

4.11 内标工作溶液:将内标元素标准储备溶液(4.8),用硝酸溶液(4.4)逐级稀释至浓度为 200  $\mu\text{g/L}$ 。

4.12 质谱调谐液:10  $\mu\text{g/L}$  Mg、Cu、Rh、Cd、In、Ba、Ce、Pb、U 溶液。

4.13 氦气、纯度 $\geq 99.99\%$ 。

## 5 仪器和设备

5.1 电感耦合等离子体质谱仪(ICP-MS)。

5.2 分析天平:感量 0.1 mg。

5.3 微波消解系统。

5.4 分析研磨机。

注:所有器皿经 50%硝酸溶液浸泡过夜。

## 6 试样制备与保存

6.1 取行代表性试样约 200 g,用分析研磨机将其制成粉末(95%以上粉末能够通过 R40/3 系列孔径为 0.71 mm 的标准试验筛),装入洁净容器,存储于干燥器中。

6.2 制样操作过程中应防止样品受到污染或发生残留物含量的变化。

## 7 样品消解

准确称取制备好的样品 0.2 g(精确至 0.000 1 g)于微波消解罐中,加入 6 mL 消解液(4.3)。设置合适的微波消解条件进行消解(参见附录 A)。消解完毕后自然冷却,将消解液过滤转移至 25 mL 容量瓶中,用水冲洗消解罐 3 次以上,定容至刻度,摇匀后备用。同时做试剂空白。

## 8 测定

8.1 分别将系列标准混合溶液导入调至最佳条件(参见附录 B)的仪器雾化系统中进行测定。以 16 种稀土元素的浓度为横坐标,以 16 种稀土元素与内标元素的强度比为纵坐标分别绘制标准曲线和计算回归方程。

8.2 分别将处理后的样品溶液、试剂空白导入调至最佳条件的仪器雾化系统中进行测定。以 16 种稀土元素与内标元素的强度比与标准曲线比较带入方程式求出含量。

## 9 结果计算

试样中稀土元素含量的计算见式(1),计算结果保留两位有效数字。

$$X = \sum_{i=1}^{16} [(c_{1i} - c_{2i})V/m]$$

.....( 1 )

式中：

$X$  —— 试样中稀土元素的含量,单位为毫克每千克(mg/kg)；

$c_{1i}$  —— 测定用试样液中稀土元素的含量,单位为毫克每升(mg/L)；

$c_{2i}$  —— 试剂空白液中稀土元素的含量,单位为毫克每升(mg/L)；

$V$  —— 试样处理液的总体积,单位为毫升(mL)；

$m$  —— 试样质量,单位为克(g)。

10 精密度

精密度范围参见附录 D。

11 检出限

见表 1。

表 1 电感耦合等离子体质谱法检出限

元素	检出限 mg/kg	元素	检出限 mg/kg	元素	检出限 mg/kg	元素	检出限 mg/kg
Sc	0.02	Y	0.01	La	0.01	Ce	0.01
Pr	0.01	Nd	0.01	Sm	0.01	Eu	0.01
Gd	0.01	Tb	0.01	Dy	0.01	Ho	0.01
Er	0.01	Tm	0.01	Yb	0.01	Lu	0.01

第二法 电感耦合等离子体发射光谱法(ICP-AES)

12 原理

用硝酸-双氧水作为消解液,将试样经过微波消解后转移定容,制得样品溶液。采用电感耦合等离子体发射光谱(ICP-AES)检测样品溶液中 16 种元素的含量,进而计算出试样中 16 种元素的含量,计算其总量。

13 试剂

- 13.1 同 4.1~4.5、4.7、4.9。
- 13.2 16 种元素标准工作溶液:分别移取 0 mL、0.5 mL、1.0 mL、2.0 mL、5.00 mL、10.0 mL 标准中间溶液(4.9),于 25 mL 的容量瓶中,用硝酸溶液(4.4)定容,混匀。此标准工件溶液中含 Sc 浓度分别为 0 μg/L、20 μg/L、40 μg/L、80 μg/L、200 μg/L、400 μg/L。含其他 15 种稀土元素浓度分别为0 μg/L、10 μg/L、20 μg/L、40 μg/L、100 μg/L、200 μg/L。该标准工作溶液均为用时现配。
- 13.3 同 4.13。



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14 仪器和设备

14.1 电感耦合等离子体发射光谱仪(ICP-AES)。

14.2 同 5.2~5.4。

15 试样制备与保存

同第 6 章。

16 样品消解

同第 7 章。

17 测定

17.1 分别将系列标准混合溶液导入调至最佳条件(参见附录 C)的仪器雾化系统中进行测定。以16 种稀土元素的浓度为横坐标,以 16 种稀土元素强度值为纵坐标分别绘制标准曲线和计算回归方程。

17.2 分别将处理后的样品溶液、试剂空白导入调至最佳条件的仪器雾化系统中进行测定。以 16 种稀土元素强度值与标准曲线比较带入方程式求出含量。

18 结果计算

按式(1)计算。

19 精密度

同第 10 章。

20 检出限

见表 2。

表 2 电感耦合等离子体发射光谱法检出限

元素	检出限 mg/kg	元素	检出限 mg/kg	元素	检出限 mg/kg	元素	检出限 mg/kg
Sc	0.20	Y	0.10	La	0.10	Ce	0.10
Pr	0.10	Nd	0.10	Sm	0.10	Eu	0.10
Gd	0.10	Tb	0.10	Dy	0.10	Ho	0.10
Er	0.10	Tm	0.10	Yb	0.10	Lu	0.10

附 录 A  
(资料性附录)  
微波消解条件

表 A.1 微波消解仪最佳消解条件<sup>1)</sup>

步骤	升温时间 min	升至温度 ℃	保持时间 min
1	5	120	10
2	5	160	10
3	5	190	20

1) 非商业性声明:表 A.1 所列参数是在 CEM MARS X-press 上完成,此处列出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厂家和型号的仪器。

附 录 B  
(资料性附录)  
ICP-MS 参考条件

表 B.1 ICP-MS 的仪器工作条件及参数<sup>2)</sup>

工作条件	参数
雾化气流量(NEB)/(L/min)	0.85
辅助气流量/(L/min)	1.2
等离子气流量/(L/min)	15
透镜电压/V	6
ICP 射频功率/W	1 200
模拟阶段的电压/V	—1 850
脉冲阶段的电压/V	950

表 B.2 选择质量数

元素	质量数	元素	质量数	元素	质量数	元素	质量数
Sc	45	Y	89	La	139	Ce	140
Pr	141	Nd	146	Sm	152	Eu	153
Gd	156	Tb	159	Dy	163	Ho	165
Er	166	Tm	169	Yb	172	Lu	175

表 B.3 内标选择质量数

内标元素	质量数
In	115

2) 非商业性声明:表 B.1 所列参数是在 PE DRC-e 上完成,此处列出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厂家和型号的仪器。

附 录 C  
(资料性附录)  
ICP-AES 参考条件

表 C.1 ICP-AES 的仪器工作条件及参数<sup>3)</sup>

工作条件	参数
功率/kW	1.00
等离子体流量/(L/min)	15.0
辅助气流量/(L/min)	1.5
雾化气流量/(L/min)	1.00

表 C.2 16 种稀土元素波长的选择

元素	波长/nm	元素	波长/nm	元素	波长/nm	元素	波长/nm
Sc	361.383	Y	371.029	La	398.852	Ce	413.765
Pr	422.293	Nd	406.108	Sm	359.259	Eu	412.972
Gd	342.246	Tb	350.914	Dy	353.171	Ho	345.600
Er	369.265	Tm	346.220	Yb	328.937	Lu	261.541

3) 非商业性声明:表 C.1 所列参数是在 AGILENT720-ES 上完成,此处列出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厂家和型号的仪器。

附录 D  
(资料性附录)  
回收率范围

表 D.1 样品中十六种稀土元素不同添加水平的回收率范围(ICP-MS)

元素	添加浓度 mg/kg	人参		紫苏叶		金银花		枸杞		麻黄		黄柏	
		回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %
Lu	0.01	72.5~94.6	7.6	72.6~100.0	8.8	72.5~91.3	9.5	72.5~91.3	9.5	78.3~103.1	8.5	72.5~100.4	9.9
	0.02	79.8~102.5	9.4	72.9~90.0	7.4	79.8~95.6	6.2	80.9~94.1	7.9	79.5~99.4	8.6	86.0~99.7	6.9
	0.10	84.6~100.6	8.0	83.8~100.1	5.9	88.9~101.2	4.7	91.8~99.6	2.9	82.5~103.1	7.3	91.8~99.6	2.9
Y	0.01	73.8~95.0	8.6	83.0~101.5	8.3	70.5~91.3	8.5	75.0~103.1	10.5	—	—	—	—
	0.02	78.4~98.6	6.7	84.3~102.4	6.2	86.0~94.9	3.1	80.9~105.5	9.2	—	—	—	—
	0.10	89.6~100.6	4.1	80.6~92.0	6.9	88.9~101.2	6.8	81.9~102.6	8.1	82.5~103.1	2.8	81.9~102.6	3.2
La	0.01	72.5~93.8	7.9	—	—	—	—	72.5~106.3	11.3	—	—	—	—
	0.02	80.5~100.6	7.6	—	—	—	—	81.4~98.5	7.2	—	—	—	—
	0.10	86.7~99.7	5.5	72.0~109.5	2.2	81.9~100.2	2.1	83.3~97.8	4.9	79.5~99.4	1.4	86.4~97.8	1.1
Ce	0.01	73.8~91.3	2.0	—	—	—	—	81.5~106.1	8.4	—	—	—	—
	0.02	79.8~95.6	2.3	—	—	—	—	89.4~98.1	3.2	—	—	—	—
	0.10	88.9~101.2	3.6	77.2~91.2	0.8	81.8~102.1	1.8	86.3~100.3	5.7	79.5~100.3	1.0	86.3~100.3	0.6
Pr	0.01	76.5~95.6	8.0	78.0~106.9	8.0	73.8~91.3	2.7	72.5~93.8	7.8	—	—	72.5~96.8	1.6
	0.02	80.5~100.6	7.9	80.5~100.5	7.9	79.8~95.6	3.8	86.0~102.8	6.3	82.5~103.1	1.7	86.4~102.8	1.7
	0.10	84.6~99.7	5.2	85.3~109.1	5.2	88.9~101.2	4.1	88.2~98.3	4.6	82.5~103.1	4.5	84.3~100.4	4.6
Nd	0.01	78.6~91.5	6.0	—	—	—	—	72.5~100.4	9.6	—	—	—	—
	0.02	81.6~100.3	8.3	—	—	—	—	81.6~102.8	7.5	—	—	—	—
	0.10	84.5~98.9	5.0	83.4~106.9	2.1	88.9~101.2	1.6	91.8~100.3	3.2	79.5~103.1	1.9	92.9~100.3	0.7



表 D.1 (续)

元素	添加浓度 mg/kg	人参		紫苏叶		金银花		枸杞		麻黄		黄柏	
		回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %
Sm	0.01	79.6~92.3	5.5	79.8~92.0	1.1	73.8~91.3	1.5	70.4~93.1	9.2	70.4~103.1	14.0	—	—
	0.02	79.8~93.6	6.9	83.2~96.5	1.6	79.8~95.6	1.7	83.3~105.6	9.4	82.5~103.1	7.3	83.3~97.3	1.3
	0.10	86.9~97.8	4.5	86.5~98.0	2.6	88.9~101.2	3.2	89.8~97.6	3.0	79.5~103.1	9.9	89.8~97.6	3.0
Eu	0.01	73.8~92.3	8.3	75.5~100.8	8.3	75.0~84.1	1.7	73.8~94.5	10.2	79.5~103.1	8.2	72.5~97.3	9.0
	0.02	79.8~100.1	7.0	79.5~101.3	7.0	81.7~92.4	2.9	80.9~95.8	6.3	82.5~103.1	8.3	82.5~95.8	5.4
	0.10	89.6~100.1	4.1	84.6~99.3	4.1	82.7~103.4	6.8	91.8~99.6	2.7	79.5~103.1	10.7	86.4~98.5	5.2
Gd	0.01	73.8~91.3	7.6	82.1~91.9	7.6	72.6~100.0	3.0	70.4~93.1	9.2	—	—	73.3~96.8	2.4
	0.02	79.8~95.6	7.8	81.0~96.7	7.8	80.2~104.6	4.4	80.9~99.8	8.2	82.5~106.5	2.2	81.4~97.9	2.7
	0.10	88.9~100.6	3.8	80.2~93.6	3.8	86.6~97.0	3.6	81.9~97.9	8.2	82.5~103.1	5.6	80.9~100.4	5.6
Tb	0.01	80.2~93.8	5.8	83.5~103.1	6.9	71.5~94.2	12.0	72.5~92.4	9.8	72.5~99.6	10.2	82.5~106.0	13.8
	0.02	81.3~96.8	5.3	86.9~103.4	5.6	82.4~97.8	7.2	83.3~106.0	10.1	79.5~99.4	8.9	83.3~105.6	9.0
	0.10	88.9~100.1	4.1	83.2~105.8	7.8	85.4~105.4	7.8	82.5~106.5	9.0	82.5~99.4	5.9	86.4~97.3	3.7
Dy	0.01	75.0~91.3	6.5	74.3~102.8	10.0	72.5~91.3	10.7	72.5~91.3	7.7	72.5~103.1	11.9	72.5~95.6	9.3
	0.02	80.5~92.3	4.9	83.2~103.1	7.6	86.9~94.2	2.8	81.6~100.3	7.1	82.5~100.3	5.7	86.3~100.3	6.2
	0.10	89.6~96.8	3.1	82.5~103.1	6.9	86.9~97.8	5.4	91.8~99.6	2.9	82.5~103.1	6.6	81.4~99.4	8.3
Ho	0.01	72.5~91.4	8.3	73.8~91.3	9.5	70.8~92.8	11.4	84.4~100.3	6.0	79.5~103.1	10.2	78.9~95.0	6.5
	0.02	76.8~97.5	4.9	82.5~95.6	6.2	82.2~101.6	7.2	81.4~100.6	9.5	82.5~103.2	6.7	80.9~100.6	9.5
	0.10	86.4~100.6	5.6	88.9~101.2	4.7	80.2~105.6	8.8	91.8~104.8	4.8	79.5~104.8	9.8	90.4~104.8	4.8
Er	0.01	72.5~100.0	9.2	71.4~103.4	12.4	71.6~91.3	8.9	72.5~91.3	8.3	81.3~103.1	10.0	72.5~91.3	8.4
	0.02	79.8~95.6	6.8	81.7~91.8	4.0	72.1~91.3	6.9	81.4~95.7	5.5	82.5~103.1	7.4	81.4~98.3	6.9
	0.10	84.5~98.5	5.8	82.5~97.5	5.1	82.4~109.2	9.8	74.5~102.0	10.7	82.5~99.4	6.3	78.4~99.5	7.6

表 D.1 (续)

元素	添加浓度 mg/kg	人参		紫苏叶		金银花		枸杞		麻黄		黄柏	
		回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %
Tm	0.01	72.5~96.3	10.3	83.2~105.8	7.8	72.5~91.3	9.5	73.8~90.6	7.9	81.3~103.1	8.9	81.3~96.8	6.3
	0.02	79.8~95.6	6.5	88.2~103.1	5.2	86.9~94.2	7.4	81.4~99.7	8.2	82.5~103.1	7.8	83.3~98.5	6.2
	0.10	89.6~100.1	4.2	82.5~97.5	6.6	86.9~97.8	7.7	84.4~100.3	6.0	79.5~104.8	9.0	87.5~100.3	7.0
Sc	0.02	78.9~95.8	6.3	80.0~101.5	7.4	78.6~94.5	6.7	74.4~91.9	8.1	77.5~103.1	11.6	75.0~93.0	8.6
	0.04	78.9~98.7	8.1	74.8~102.5	9.9	75.1~88.1	4.8	86.3~102.5	6.5	82.5~103.7	7.7	75.0~102.5	12.2
	0.20	84.5~102.3	6.7	81.2~100.9	6.8	86.9~100.3	5.7	84.5~100.2	5.0	82.5~104.1	7.0	91.8~100.2	3.2
Yb	0.01	72.5~94.6	8.3	—	—	72.5~95.6	9.0	85.0~104.8	6.6	82.5~103.0	7.1	86.3~98.3	6.9
	0.02	79.8~94.2	5.9	—	—	85.0~99.4	5.1	81.3~97.9	6.7	82.5~102.9	7.5	81.3~100.6	7.0
	0.10	85.0~101.2	5.4	76.4~100.1	3.4	85.1~102.5	7.0	84.1~98.6	5.4	81.5~103.1	8.1	81.3~98.6	6.9

表 D.2 样品中十六种稀土元素不同添加水平的回收率范围 (ICP-AES)

元素	添加浓度 mg/kg	人参		紫苏叶		金银花		枸杞		麻黄		黄柏	
		回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %
Lu	0.1	72.5~94.8	9.6	71.8~92.6	8.8	76.5~98.5	8.6	72.5~91.3	9.5	72.5~94.1	8.3	74.4~100.9	9.1
	0.2	76.8~95.6	6.8	77.5~95.6	7.4	78.9~94.6	5.7	80.9~99.7	7.9	80.9~94.1	6.0	80.9~99.7	8.3
	1.0	84.6~102.6	6.4	84.6~100.4	5.9	84.6~98.5	5.7	91.8~99.6	2.9	80.9~99.7	7.9	81.4~99.6	7.2
Y	0.1	75.6~97.8	8.6	77.5~97.5	8.3	77.5~93.2	7.0	75.0~103.1	10.5	75.0~103.1	4.4	75.0~105.5	4.0
	0.2	78.9~94.7	7.1	80.4~94.2	6.2	80.4~100.2	6.7	81.0~105.5	8.7	84.6~99.6	2.8	75.0~98.3	5.1
	1.0	86.4~105.6	6.6	80.1~99.5	6.9	80.4~100.1	7.1	81.9~102.6	9.2	81.9~86.9	2.0	81.9~106.3	8.2
La	0.1	72.5~91.5	8.1	72.5~98.5	2.0	75.6~100.8	2.8	85.0~106.3	7.3	72.8~92.8	2.1	90.4~99.4	0.8
	0.2	79.8~94.8	5.9	77.5~104.2	3.2	80.6~100.9	3.9	83.3~107.1	8.2	83.3~107.1	2.7	83.3~107.1	3.1
	1.0	86.4~105.6	6.4	86.4~102.3	4.5	78.9~104.5	7.2	85.0~93.8	2.9	85.0~93.8	2.1	85.0~93.8	2.1



表 D.2 (续)

元素	添加浓度 mg/kg	人参		紫苏叶		金银花		枸杞		麻黄		黄柏	
		回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %
Ce	0.1	74.5~102.0	11.0	73.8~102.5	1.5	78.6~100.3	1.5	71.1~89.1	8.0	—	—	—	—
	0.2	86.3~102.3	5.9	79.8~92.3	1.5	79.8~98.4	2.3	87.5~100.3	6.0	78.5~99.5	1.6	84.5~102.5	1.5
	1.0	87.9~104.8	6.4	88.7~101.2	3.4	79.8~102.4	5.6	80.0~101.6	8.6	86.1~101.6	4.2	86.3~102.5	3.6
Pr	0.1	78.5~91.3	9.2	76.5~98.4	9.4	80.2~97.6	7.8	86.0~102.8	6.3	84.6~98.7	5.7	88.4~102.8	4.8
	0.2	81.6~94.8	6.4	80.5~94.7	7.3	80.1~93.6	5.6	84.3~100.4	6.6	84.3~100.4	6.2	84.3~100.4	7.2
	1.0	86.4~96.8	4.4	80.6~100.6	7.4	83.4~94.6	4.1	92.3~100.3	3.1	82.5~103.1	7.0	92.5~102.8	3.9
Nd	0.1	72.5~88.5	7.4	76.4~96.5	2.6	78.4~94.9	2.1	70.4~93.1	9.2	70.4~93.1	1.6	74.7~93.8	1.6
	0.2	82.4~98.7	6.5	81.6~97.1	2.7	81.6~97.6	3.6	82.4~98.7	6.5	85.6~101.7	1.9	82.0~98.7	2.4
	1.0	86.4~103.7	5.6	84.6~97.8	3.7	84.6~97.8	4.6	86.4~103.7	5.6	86.4~103.7	4.0	86.4~103.7	3.9
Sm	0.1	78.4~102.5	9.6	78.5~90.5	4.8	75.6~98.4	10.1	85.0~106.3	7.3	74.7~98.5	10.5	77.6~97.0	8.0
	0.2	80.4~94.2	5.7	80.4~92.3	5.7	79.8~100.2	8.1	81.9~105.6	9.4	83.3~100.4	7.7	81.9~105.6	10.5
	1.0	86.4~101.6	5.6	83.5~99.4	6.5	84.2~98.6	6.7	85.0~93.8	2.9	91.3~98.5	3.0	81.9~105.7	8.2
Eu	0.1	75.4~96.7	8.5	77.5~100.2	8.9	76.4~100.1	9.6	73.8~94.8	9.5	75.6~105.6	10.5	73.8~94.8	9.5
	0.2	78.9~94.7	6.5	80.4~95.6	5.9	78.9~98.7	9.2	83.3~107.1	8.2	83.3~107.1	8.2	81.3~99.6	7.1
	1.0	86.4~105.6	6.4	89.4~102.3	4.7	80.4~104.6	8.2	89.8~97.6	3.0	81.3~97.0	5.2	81.3~97.0	5.1
Gd	0.1	73.8~94.8	9.5	75.6~94.4	9.2	75.6~93.8	7.6	72.5~90.5	9.8	72.5~95.4	10.0	72.5~106.5	11.3
	0.2	82.0~105.6	8.5	78.7~95.6	6.5	81.6~102.0	6.5	82.5~106.0	9.1	82.5~106.5	9.6	81.9~105.6	9.3
	1.0	87.7~102.6	5.3	81.9~94.5	4.9	82.6~101.9	8.0	82.5~106.5	9.0	82.5~106.5	9.0	82.5~105.6	9.3
Tb	0.1	71.9~96.4	9.0	76.1~91.5	7.7	77.8~96.5	7.8	81.3~99.4	7.5	70.4~92.3	8.8	82.7~99.4	6.4
	0.2	79.8~100.9	8.7	79.8~103.7	9.1	79.8~96.4	6.5	78.9~107.1	9.6	78.9~107.1	9.8	82.5~107.1	8.4
	1.0	84.6~103.2	6.5	87.6~99.3	4.0	87.8~97.8	3.8	82.0~92.5	4.3	89.6~97.9	3.3	81.3~97.3	5.0

表 D.2 (续)

元素	添加浓度 mg/kg	人参		紫苏叶		金银花		枸杞		麻黄		黄柏	
		回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %	回收率 %	RSD %
Dy	0.1	72.5~91.3	9.5	72.5~91.3	9.5	76.8~100.2	10.7	78.5~98.5	10.4	92.9~99.6	2.1	80.9~100.6	9.4
	0.2	79.8~95.6	6.2	79.8~95.6	6.2	76.7~100.8	8.9	86.3~107.1	7.8	84.4~100.3	5.8	86.3~107.1	7.4
	1.0	88.9~101.2	4.7	87.6~101.2	5.0	87.4~98.4	4.7	89.6~104.8	5.5	89.6~104.8	5.5	89.6~100.6	5.0
Ho	0.1	73.8~94.8	9.5	75.6~100.2	10.1	75.6~93.8	5.2	78.4~99.5	10.0	78.4~99.5	9.1	78.9~99.7	11.3
	0.2	76.8~97.5	6.9	76.8~100.3	10.0	81.6~102.0	5.8	78.9~103.2	8.1	74.5~102.0	8.6	78.4~94.9	7.1
	1.0	84.6~103.2	2.9	84.6~100.4	6.7	82.6~101.9	4.8	89.6~104.8	6.3	81.4~99.7	7.2	80.1~104.8	8.1
Er	0.1	73.8~97.4	10.0	73.8~91.3	7.3	73.8~90.2	6.4	73.8~98.5	10.9	74.5~102.0	10.5	78.4~98.5	9.7
	0.2	78.9~106.4	6.2	78.9~102.3	6.2	80.6~100.2	8.1	86.4~107.1	8.8	85.2~107.1	8.7	74.5~107.1	11.8
	1.0	88.9~102.3	4.6	82.1~102.3	7.8	84.2~102.1	6.9	89.5~100.6	4.5	84.5~98.0	4.3	86.4~105.6	6.6
Tm	0.1	72.3~98.5	9.5	72.3~100.5	10.2	79.5~100.1	8.1	74.5~102.0	10.9	75.9~97.9	8.1	74.5~102.0	11.9
	0.2	78.9~100.6	8.5	79.8~98.4	7.3	83.2~94.6	5.6	78.9~103.2	9.2	74.5~102.0	9.6	78.9~98.5	8.7
	1.0	86.4~103.2	6.4	88.6~100.2	3.7	88.6~100.2	3.7	86.4~101.7	6.4	86.3~101.7	6.1	84.5~101.7	6.5
Sc	0.2	73.8~94.6	9.7	73.8~93.8	8.1	75.8~94.6	8.4	78.5~99.5	9.1	86.3~104.8	6.4	77.5~99.5	9.7
	0.4	78.9~105.6	8.9	80.2~99.6	7.1	79.8~92.3	5.5	86.3~107.1	8.0	86.3~107.1	7.5	84.5~107.1	8.4
	2.0	88.9~102.3	5.6	87.7~99.7	5.2	84.6~100.5	3.2	87.8~104.8	5.8	89.6~104.8	5.7	90.6~104.8	5.0
Yb	0.1	74.8~99.5	9.5	78.5~90.1	1.7	78.5~97.8	8.3	80.1~100.6	7.3	75.9~98.3	8.1	86.3~100.6	6.7
	0.2	79.8~103.2	9.2	81.4~100.2	4.0	80.9~98.4	7.0	75.9~100.6	9.6	89.6~99.4	4.6	86.3~99.4	5.4
	1.0	85.2~105.6	7.7	85.2~98.5	4.3	83.8~98.6	6.4	89.6~101.7	4.6	89.6~96.8	2.5	86.3~97.9	4.3

## Foreword

This standard was drafted according to GB/T 1.1—2009.

Please note that some of the elements of this document may be involved in patent, issued the document does not assume the responsibility identification of these patents.

This standard was proposed by and was under the charge of National Regulatory Commission for Certification and Accreditation of the People's Republic of China.

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

This standard was mainly drafted by Wang Jing, Zhu Meiwen, Wang Junsu, Peng Guangyu, Zheng Guocan, Chen Jiang.

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**Note:** This English version, a translation from the Chinese text, is solely for guidance.



# Determination of rare earth elements in botanic Chinese medicinal material for export

## 1 Scope

The standard specifies the methods of ICP-MS & ICP-AES determination of rare earth elements in botanic Chinese medicinal material for export.

This standard is applicable to the determination of rare earth elements in botanic Chinese medicinal material such as ginseng, basil leaves, honeysuckle, wolfberry, ephedra, treats.

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 602 Chemical reagent—Preparations of standard solutions for impurity

GB/T 6682 Water for analytical laboratory use—Specification and test method

The first method Inductively coupled plasma mass spectrometry method (ICP-MS)

## 3 Principle

Using nitric acid and hydrogen peroxide as digestion solution, samples are digested by sealed microwave. 16 kinds of rare earth elements in the sample solution are detected by the inductively coupled plasma mass spectrometry (ICP-MS), calculate the total.

## 4 Reagents and materials

Unless otherwise specified, all the reagent used should be high pure. And the water shall comply with the requirement of GB/T 6682 (first class water).

4.1 Nitric acid.

4.2 30% Hydrogen peroxide.

4.3 Digestion solution: mixed 2 parts of nitric acid(4.1) and 1 part of hydrogen peroxide(4.2), cooling.

4.4 Nitric acid(1%, V/V): dilute 10 mL nitric acid(4.1) to 1 000 mL with water.

4.5 16 kinds of standard solution: Sc concentration of standard solution 1 000 mg/L(4.5.1), Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu (hereinafter referred to as the other 15 kinds of rare-earth) mixed standard solution concentration of 100 mg/L(4.5.2). Prepared by the GB/T 602, or direct use the certified reference materials.

4.6 Internal standards solution (In): 1 000 mg/L. Prepared by the GB/T 602, or direct use the certified reference materials.

4.7 Mixed standard stock solution: Accurately pipette 2.0 mL Sc standard solution (4.5.1) and 10.0 mL the other 15 kinds of rare-earth standard solution (4.5.2) then transfer it into 100 mL volumetric flask, dilute to mark with nitric acid (4.4). The solution concentration is Sc 20 mg/L and other 15 kinds of rare-earth 10 mg/L.

4.8 Internal standards stock solution: Accurately pipette 1.0 mL internal standard solution (4.6), transfer it into 100 mL volumetric flask, dilute to mark with nitric acid(4.4). The solution concentration is 10 mg/L.

4.9 Mixed standard intermediate solution: Accurately pipette mixed standard stock solution(4.7) 5 mL transfer in into 100 mL volumetric flask, dilute to mark with nitric acid (4.4). The solution concentration is Sc 1 000 µg/L, other 15 kinds of rare-earth 500 µg/L.

4.10 Mixed standard working solution: Accurately pipette mixed standard intermediate solution (4.9) respectively 0 mL, 0.5 mL, 1.0 mL, 2.0 mL, 5.0 mL, 10.0 mL into 100 mL volumetric flask, dilute to mark with nitric acid (4.4) to get the mixed standard working solution with the Sc concentration is 0 µg/L, 5 µg/L, 10 µg/L, 20 µg/L, 50 µg/L, 100 µg/L, other 15 kinds of rare-earth concentration is 0 µg/L, 2.5 µg/L, 5 µg/L, 10 µg/L, 25 µg/L, 50 µg/L.

4.11 Internal standards working solution: Gradually diluted Internal standards stock solution(4.8) to the concentration of 200 µg/L with nitric acid(4.4).

4.12 Tune solution: 10 µg/L Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U mixed solution.

4.13 Liquid argon or high purity argon: purity ≥ 99.99%.

## 5 Apparatus and equipment

5.1 Inductively coupled plasma mass spectrometry (ICP-MS).

5.2 Balance: with 0.000 1 g sensitivity.

5.3 Sealed microwave digest device.

5.4 Grinding machine.

**Note:** All vessels could be soaked in 50% nitric acid solution for more than 12 h.

## 6 Sample preparation and preservation

6.1 Take a representative sample of about 200 g, and make it into powder with the grinding machine (more than 95% powder can pass R40/3 series standard test sieve with the pore size of 0.71 mm), then loaded the powder into a clean container, stored in a dryer.

6.2 The test sample shall avoid contaminations and changes of residue content during the preparing process.

## 7 Test sample digestion

Weigh 0.2 g sample into microwave digest vessel, add 6 mL digestion solution (4.3), seal the vessel and put it into sealed microwave digest device (5.3), set the suitable digestion program and start digestion (the working conditions are listed in appendix A). After digestion finish, cool it, open the vessel, transfer the digestion solution into 25 mL comparison tube, flush the vessel more than 3 times and then add water to 25 mL and mix them well. A blank test is done in parallel with the sample digestion. The sample solution can be diluted appropriately according to the practical content of analytical element and the diluted factors can be calculated.

## 8 Determination

### 8.1 The test conditions of instrument

According to the equipment operating procedures, adjust the working conditions of the instrument (the working conditions are listed in appendix B).

### 8.2 Analysis

Use internal standards quantitative analysis method. According to the 8.1 the test conditions of in-



strument, establish the calibration by mixed standard working solution, then detect the sample solution in the same conditions.

## 9 Expression of results

The content of rare-earth elements is calculated according to the formula (1), the results express as the number with 2 significant digits.

$$X = \sum_{i=1}^{16} [(c_{1i} - c_{2i}) V / m] \quad \dots\dots\dots (1)$$

Where:

$X$  —the content of rare-earth elements in test sample, mg/kg;

$c_{1i}$  —the concentration of the analytical element in testing solution, mg/L;

$c_{2i}$  —the concentration of the analytical element in blank solution, mg/L;

$V$  —the volume of the testing solution, mL;

$m$  —the the mass of the test sample, g.

## 10 RSD

RSD in appendix D.

## 11 The limit of detection

seeing table 1.

Table 1—The limit of detection(ICP-MS)

element	The limit of detection mg/kg	element	The limit of detection mg/kg	element	The limit of detection mg/kg	element	The limit of detection mg/kg
Sc	0.02	Y	0.01	La	0.01	Ce	0.01
Pr	0.01	Nd	0.01	Sm	0.01	Eu	0.01
Gd	0.01	Tb	0.01	Dy	0.01	Ho	0.01
Er	0.01	Tm	0.01	Yb	0.01	Lu	0.01

## The second method Inductively coupled plasma atomic emission spectrometer method(ICP-AES)

### 12 Principle

Using nitric acid and hydrogen peroxide as digestion solution, samples are digested by sealed microwave. 16 kinds of rare earth elements in the sample solution are detected by the inductively coupled plasma atomic emission spectrometer method (ICP-AES), calculate the total.

### 13 Reagents and materials

13.1 In accordance with the content of 4.1~4.5,4.7,4.9.

13.2 Mixed standard working solution: Accurately pipette mixed standard intermediate solution (4.9) respectively 0 mL,0.5 mL,1.0 mL, 2.0 mL,5.0 mL,10.0 mL into 25 mL volumetric flask, dilute to mark with nitric acid(4.4) to get the mixed standard working solution with the Sc concentration is 0 µg/L,20 µg/L,40 µg/L,80 µg/L,200 µg/L,400 µg/L, other 15 kinds of rare-earth concentration is 0 µg/L,10 µg/L,20 µg/L,40 µg/L,100 µg/L,200 µg/L.

13.3 In accordance with the content of 4.13.

### 14 Apparatus and equipment

14.1 Inductively coupled plasma atomic emission spectrometer method (ICP-AES).

14.2 In accordance with the content of 5.2~5.4.

### 15 Sample preparation and preservation

In accordance with the content of the sixth chapter.

### 16 Determination

In accordance with the content of the seventh chapter.

## 17 Determination

### 17.1 The test conditions of instrument

According to the equipment operating procedures, adjust the working conditions of the instrument (the working conditions are listed in appendix C).

### 17.2 Analysis

Use internal standards quantitative analysis method. According to the 17.1 the test conditions of instrument, establish the calibration by mixed standard working solution, then detect the sample solution in the same conditions.

## 18 Expression of results

The content of rare-earth elements is calculated according to the formula (1), the results express as the number with 2 significant digits.

## 19 RSD

In accordance with the content of the tenth chapter.

## 20 The limit of detection

Seeing table 2.

Table 2—The limit of detection(ICP-AES)

element	The limit of detection mg/kg	element	The limit of detection mg/kg	element	The limit of detection mg/kg	element	The limit of detection mg/kg
Sc	0.20	Y	0.10	La	0.10	Ce	0.10
Pr	0.10	Nd	0.10	Sm	0.10	Eu	0.10
Gd	0.10	Tb	0.10	Dy	0.10	Ho	0.10
Er	0.10	Tm	0.10	Yb	0.10	Lu	0.10

**Annex A**  
**(Informative)**  
**The conditions of microwave digestion**

**Tab.A.1—Optimal digestion conditions of microwave digestion instrument<sup>1)</sup>**

Procedure	Heating-up time min	Temperature ℃	Retention time min
1	5	120	10
2	5	160	10
3	5	190	20

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1) Non-commercial statement: the parameters in Tab.A.1 are accomplished by CEM MARS X-press, the equipment and its type involved in the standard method is only for reference and not related to any commercial aim, and the analysts are encouraged to use equipments of different corporation or different type.

**Annex B**  
(Informative)  
**The condition of ICP-MS**

**Tab.B.1—Working conditions and parameters of ICP-MS<sup>2)</sup>**

Description	Current Value
Nebulizer Gas Flow(NEB)/(L/min)	0.85
Auxiliary Gas Flow/(L/min)	1.2
Plasma Gas Flow/(L/min)	15
Lens Voltage/V	6
ICP RF Power/W	1 200
Analog Stage Voltage/V	– 1 850
Pulse Stage Voltage/V	950

**Tab.B.2—The mass of elements**

Elements	Mass	Elements	Mass	Elements	Mass	Elements	Mass
Sc	45	Y	89	La	139	Ce	140
Pr	141	Nd	146	Sm	152	Eu	153
Gd	156	Tb	159	Dy	163	Ho	165
Er	166	Tm	169	Yb	172	Lu	175

**Tab.B.3—The mass of internal standard element**

Internal standard element	Mass
In	115

- 2) Non-commercial statement: the parameters in Tab. B. 1 are accomplished by PE DRC-e inductively coupled plasma mass spectrometry, the equipment and its type involved in the standard method is only for reference and not related to any commercial aim, and the analysts are encouraged to use equipments of different corporation of different type.



## Annex C

### (Informative)

#### The condition of ICP-AES

Tab.C.1—Working conditions and parameters of ICP-AES<sup>3)</sup>

Procedure	Recommended values
ICP RF Power/kW	1.00
Plasma Gas Flow/(L/min)	15.0
Auxiliary Gas Flow/(L/min)	1.5
Nebulizer Gas Flow/(L/min)	1.00

Tab.C.2—The wavelength of elements

Element	Wavelength nm	Element	Wavelength nm	Element	Wavelength nm	Element	Wavelength nm
Sc	361.383	Y	371.029	La	398.852	Ce	413.765
Pr	422.293	Nd	406.108	Sm	359.259	Eu	412.972
Gd	342.246	Tb	350.914	Dy	353.171	Ho	345.600
Er	369.265	Tm	346.220	Yb	328.937	Lu	261.541

3) Non-commercial statement: the parameters in Tab. C. 1 are accomplished by AGILENT 720-ES inductively coupled plasma atomic emission spectrometer method (ICP-AES), the equipment and its type involved in the standard method is only for reference and not related to any commercial aim, and the analysts are encouraged to use equipments of different corporation or different type.

**Annex D**  
(Informative)  
**Recoveries**

**Tab.D.1—Recoveries of 16 rare earth elements in botanic Chinese medicinal material(ICP-MS)**

Elements	Spiking levels mg/kg	Ginseng		Basil leaves		Honeysuckle		Wolfberry		Ephedra		Treats	
		Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %
Lu	0.01	72.5~94.6	7.6	72.6~100.0	8.8	72.5~91.3	9.5	72.5~91.3	9.5	78.3~103.1	8.5	72.5~100.4	9.9
	0.02	79.8~102.5	9.4	72.9~90.0	7.4	79.8~95.6	6.2	80.9~94.1	7.9	79.5~99.4	8.6	86.0~99.7	6.9
	0.10	84.6~100.6	8.0	83.8~100.1	5.9	88.9~101.2	4.7	91.8~99.6	2.9	82.5~103.1	7.3	91.8~99.6	2.9
Y	0.01	73.8~95.0	8.6	83.0~101.5	8.3	70.5~91.3	8.5	75.0~103.1	10.5	—	—	—	—
	0.02	78.4~98.6	6.7	84.3~102.4	6.2	86.0~94.9	3.1	80.9~105.5	9.2	—	—	—	—
	0.10	89.6~100.6	4.1	80.6~92.0	6.9	88.9~101.2	6.8	81.9~102.6	8.1	82.5~103.1	2.8	81.9~102.6	3.2
La	0.01	72.5~93.8	7.9	—	—	—	—	72.5~106.3	11.3	—	—	—	—
	0.02	80.5~100.6	7.6	—	—	—	—	81.4~98.5	7.2	—	—	—	—
	0.10	86.7~99.7	5.5	72.0~109.5	2.2	81.9~100.2	2.1	83.3~97.8	4.9	79.5~99.4	1.4	86.4~97.8	1.1
Ce	0.01	73.8~91.3	2.0	—	—	—	—	81.5~106.1	8.4	—	—	—	—
	0.02	79.8~95.6	2.3	—	—	—	—	89.4~98.1	3.2	—	—	—	—
	0.10	88.9~101.2	3.6	77.2~91.2	0.8	81.8~102.1	1.8	86.3~100.3	5.7	79.5~100.3	1.0	86.3~100.3	0.6
Pr	0.01	76.5~95.6	8.0	78.0~106.9	8.0	73.8~91.3	2.7	72.5~93.8	7.8	—	—	72.5~96.8	1.6
	0.02	80.5~100.6	7.9	80.5~100.5	7.9	79.8~95.6	3.8	86.0~102.8	6.3	82.5~103.1	1.7	86.4~102.8	1.7
	0.10	84.6~99.7	5.2	85.3~109.1	5.2	88.9~101.2	4.1	88.2~98.3	4.6	82.5~103.1	4.5	84.3~100.4	4.6
Nd	0.01	78.6~91.5	6.0	—	—	—	—	72.5~100.4	9.6	—	—	—	—
	0.02	81.6~100.3	8.3	—	—	—	—	81.6~102.8	7.5	—	—	—	—
	0.10	84.5~98.9	5.0	83.4~106.9	2.1	88.9~101.2	1.6	91.8~100.3	3.2	79.5~103.1	1.9	92.9~100.3	0.7

Tab.D.1 (continued)

Elements	Spiking levels mg/kg	Ginseng		Basil leaves		Honeysuckle		Wolfberry		Ephedra		Treats	
		Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %
Sm	0.01	79.6~92.3	5.5	79.8~92.0	1.1	73.8~91.3	1.5	70.4~93.1	9.2	70.4~103.1	14.0	—	—
	0.02	79.8~93.6	6.9	83.2~96.5	1.6	79.8~95.6	1.7	83.3~105.6	9.4	82.5~103.1	7.3	83.3~97.3	1.3
	0.10	86.9~97.8	4.5	86.5~98.0	2.6	88.9~101.2	3.2	89.8~97.6	3.0	79.5~103.1	9.9	89.8~97.6	3.0
Eu	0.01	73.8~92.3	8.3	75.5~100.8	8.3	75.0~84.1	1.7	73.8~94.5	10.2	79.5~103.1	8.2	72.5~97.3	9.0
	0.02	79.8~100.1	7.0	79.5~101.3	7.0	81.7~92.4	2.9	80.9~95.8	6.3	82.5~103.1	8.3	82.5~95.8	5.4
	0.10	89.6~100.1	4.1	84.6~99.3	4.1	82.7~103.4	6.8	91.8~99.6	2.7	79.5~103.1	10.7	86.4~98.5	5.2
Gd	0.01	73.8~91.3	7.6	82.1~91.9	7.6	72.6~100.0	3.0	70.4~93.1	9.2	—	—	73.3~96.8	2.4
	0.02	79.8~95.6	7.8	81.0~96.7	7.8	80.2~104.6	4.4	80.9~99.8	8.2	82.5~106.5	2.2	81.4~97.9	2.7
	0.10	88.9~100.6	3.8	80.2~93.6	3.8	86.6~97.0	3.6	81.9~97.9	8.2	82.5~103.1	5.6	80.9~100.4	5.6
Tb	0.01	80.2~93.8	5.8	83.5~103.1	6.9	71.5~94.2	12.0	72.5~92.4	9.8	72.5~99.6	10.2	82.5~106.0	13.8
	0.02	81.3~96.8	5.3	86.9~103.4	5.6	82.4~97.8	7.2	83.3~106.0	10.1	79.5~99.4	8.9	83.3~105.6	9.0
	0.10	88.9~100.1	4.1	83.2~105.8	7.8	85.4~105.4	7.8	82.5~106.5	9.0	82.5~99.4	5.9	86.4~97.3	3.7
Dy	0.01	75.0~91.3	6.5	74.3~102.8	10.0	72.5~91.3	10.7	72.5~91.3	7.7	72.5~103.1	11.9	72.5~95.6	9.3
	0.02	80.5~92.3	4.9	83.2~103.1	7.6	86.9~94.2	2.8	81.6~100.3	7.1	82.5~100.3	5.7	86.3~100.3	6.2
	0.10	89.6~96.8	3.1	82.5~103.1	6.9	86.9~97.8	5.4	91.8~99.6	2.9	82.5~103.1	6.6	81.4~99.4	8.3
Ho	0.01	72.5~91.4	8.3	73.8~91.3	9.5	70.8~92.8	11.4	84.4~100.3	6.0	79.5~103.1	10.2	78.9~95.0	6.5
	0.02	76.8~97.5	4.9	82.5~95.6	6.2	82.2~101.6	7.2	81.4~100.6	9.5	82.5~103.2	6.7	80.9~100.6	9.5
	0.10	86.4~100.6	5.6	88.9~101.2	4.7	80.2~105.6	8.8	91.8~104.8	4.8	79.5~104.8	9.8	90.4~104.8	4.8
Er	0.01	72.5~100.0	9.2	71.4~103.4	12.4	71.6~91.3	8.9	72.5~91.3	8.3	81.3~103.1	10.0	72.5~91.3	8.4
	0.02	79.8~95.6	6.8	81.7~91.8	4.0	72.1~91.3	6.9	81.4~95.7	5.5	82.5~103.1	7.4	81.4~98.3	6.9
	0.10	84.5~98.5	5.8	82.5~97.5	5.1	82.4~109.2	9.8	74.5~102.0	10.7	82.5~99.4	6.3	78.4~99.5	7.6



Tab.D.1 (continued)

Elements	Spiking levels mg/kg	Ginseng		Basil leaves		Honeysuckle		Wolfberry		Ephedra		Treats	
		Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %
Tm	0.01	72.5~96.3	10.3	83.2~105.8	7.8	72.5~91.3	9.5	73.8~90.6	7.9	81.3~103.1	8.9	81.3~96.8	6.3
	0.02	79.8~95.6	6.5	88.2~103.1	5.2	86.9~94.2	7.4	81.4~99.7	8.2	82.5~103.1	7.8	83.3~98.5	6.2
	0.10	89.6~100.1	4.2	82.5~97.5	6.6	86.9~97.8	7.7	84.4~100.3	6.0	79.5~104.8	9.0	87.5~100.3	7.0
Sc	0.02	78.9~95.8	6.3	80.0~101.5	7.4	78.6~94.5	6.7	74.4~91.9	8.1	77.5~103.1	11.6	75.0~93.0	8.6
	0.04	78.9~98.7	8.1	74.8~102.5	9.9	75.1~88.1	4.8	86.3~102.5	6.5	82.5~103.7	7.7	75.0~102.5	12.2
	0.20	84.5~102.3	6.7	81.2~100.9	6.8	86.9~100.3	5.7	84.5~100.2	5.0	82.5~104.1	7.0	91.8~100.2	3.2
Yb	0.01	72.5~94.6	8.3	—	—	72.5~95.6	9.0	85.0~104.8	6.6	82.5~103.0	7.1	86.3~98.3	6.9
	0.02	79.8~94.2	5.9	—	—	85.0~99.4	5.1	81.3~97.9	6.7	82.5~102.9	7.5	81.3~100.6	7.0
	0.10	85.0~101.2	5.4	76.4~100.1	3.4	85.1~102.5	7.0	84.1~98.6	5.4	81.5~103.1	8.1	81.3~98.6	6.9

Tab.D.2—Recoveries of 16 rare earth elements in botanic Chinese medicinal material(ICP-AES)

Elements	Spiking levels mg/kg	Ginseng		Basil leaves		Honeysuckle		Wolfberry		Ephedra		Treats	
		Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %
Lu	0.1	72.5~94.8	9.6	71.8~92.6	8.8	76.5~98.5	8.6	72.5~91.3	9.5	72.5~94.1	8.3	74.4~100.9	9.1
	0.2	76.8~95.6	6.8	77.5~95.6	7.4	78.9~94.6	5.7	80.9~99.7	7.9	80.9~94.1	6.0	80.9~99.7	8.3
	1.0	84.6~102.6	6.4	84.6~100.4	5.9	84.6~98.5	5.7	91.8~99.6	2.9	80.9~99.7	7.9	81.4~99.6	7.2
Y	0.1	75.6~97.8	8.6	77.5~97.5	8.3	77.5~93.2	7.0	75.0~103.1	10.5	75.0~103.1	4.4	75.0~105.5	4.0
	0.2	78.9~94.7	7.1	80.4~94.2	6.2	80.4~100.2	6.7	81.0~105.5	8.7	84.6~99.6	2.8	75.0~98.3	5.1
	1.0	86.4~105.6	6.6	80.1~99.5	6.9	80.4~100.1	7.1	81.9~102.6	9.2	81.9~86.9	2.0	81.9~106.3	8.2
La	0.1	72.5~91.5	8.1	72.5~98.5	2.0	75.6~100.8	2.8	85.0~106.3	7.3	72.8~92.8	2.1	90.4~99.4	0.8
	0.2	79.8~94.8	5.9	77.5~104.2	3.2	80.6~100.9	3.9	83.3~107.1	8.2	83.3~107.1	2.7	83.3~107.1	3.1
	1.0	86.4~105.6	6.4	86.4~102.3	4.5	78.9~104.5	7.2	85.0~93.8	2.9	85.0~93.8	2.1	85.0~93.8	2.1

Tab.D.2 (continued)

Elements	Spiking levels mg/kg	Ginseng		Basil leaves		Honeysuckle		Wolfberry		Ephedra		Treats	
		Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %
Ce	0.1	74.5~102.0	11.0	73.8~102.5	1.5	78.6~100.3	1.5	71.1~89.1	8.0	—	—	—	—
	0.2	86.3~102.3	5.9	79.8~92.3	1.5	79.8~98.4	2.3	87.5~100.3	6.0	78.5~99.5	1.6	84.5~102.5	1.5
	1.0	87.9~104.8	6.4	88.7~101.2	3.4	79.8~102.4	5.6	80.0~101.6	8.6	86.1~101.6	4.2	86.3~102.5	3.6
Pr	0.1	78.5~91.3	9.2	76.5~98.4	9.4	80.2~97.6	7.8	86.0~102.8	6.3	84.6~98.7	5.7	88.4~102.8	4.8
	0.2	81.6~94.8	6.4	80.5~94.7	7.3	80.1~93.6	5.6	84.3~100.4	6.6	84.3~100.4	6.2	84.3~100.4	7.2
	1.0	86.4~96.8	4.4	80.6~100.6	7.4	83.4~94.6	4.1	92.3~100.3	3.1	82.5~103.1	7.0	92.5~102.8	3.9
Nd	0.1	72.5~88.5	7.4	76.4~96.5	2.6	78.4~94.9	2.1	70.4~93.1	9.2	70.4~93.1	1.6	74.7~93.8	1.6
	0.2	82.4~98.7	6.5	81.6~97.1	2.7	81.6~97.6	3.6	82.4~98.7	6.5	85.6~101.7	1.9	82.0~98.7	2.4
	1.0	86.4~103.7	5.6	84.6~97.8	3.7	84.6~97.8	4.6	86.4~103.7	5.6	86.4~103.7	4.0	86.4~103.7	3.9
Sm	0.1	78.4~102.5	9.6	78.5~90.5	4.8	75.6~98.4	10.1	85.0~106.3	7.3	74.7~98.5	10.5	77.6~97.0	8.0
	0.2	80.4~94.2	5.7	80.4~92.3	5.7	79.8~100.2	8.1	81.9~105.6	9.4	83.3~100.4	7.7	81.9~105.6	10.5
	1.0	86.4~101.6	5.6	83.5~99.4	6.5	84.2~98.6	6.7	85.0~93.8	2.9	91.3~98.5	3.0	81.9~105.7	8.2
Eu	0.1	75.4~96.7	8.5	77.5~100.2	8.9	76.4~100.1	9.6	73.8~94.8	9.5	75.6~105.6	10.5	73.8~94.8	9.5
	0.2	78.9~94.7	6.5	80.4~95.6	5.9	78.9~98.7	9.2	83.3~107.1	8.2	83.3~107.1	8.2	81.3~99.6	7.1
	1.0	86.4~105.6	6.4	89.4~102.3	4.7	80.4~104.6	8.2	89.8~97.6	3.0	81.3~97.0	5.2	81.3~97.0	5.1
Gd	0.1	73.8~94.8	9.5	75.6~94.4	9.2	75.6~93.8	7.6	72.5~90.5	9.8	72.5~95.4	10.0	72.5~106.5	11.3
	0.2	82.0~105.6	8.5	78.7~95.6	6.5	81.6~102.0	6.5	82.5~106.0	9.1	82.5~106.5	9.6	81.9~105.6	9.3
	1.0	87.7~102.6	5.3	81.9~94.5	4.9	82.6~101.9	8.0	82.5~106.5	9.0	82.5~106.5	9.0	82.5~105.6	9.3
Tb	0.1	71.9~96.4	9.0	76.1~91.5	7.7	77.8~96.5	7.8	81.3~99.4	7.5	70.4~92.3	8.8	82.7~99.4	6.4
	0.2	79.8~100.9	8.7	79.8~103.7	9.1	79.8~96.4	6.5	78.9~107.1	9.6	78.9~107.1	9.8	82.5~107.1	8.4
	1.0	84.6~103.2	6.5	87.6~99.3	4.0	87.8~97.8	3.8	82.0~92.5	4.3	89.6~97.9	3.3	81.3~97.3	5.0



Tab.D.2 (continued)

Elements	Spiking levels mg/kg	Ginseng		Basil leaves		Honeysuckle		Wolfberry		Ephedra		Treats	
		Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %	Recoveries %	RSD %
Dy	0.1	72.5~91.3	9.5	72.5~91.3	9.5	76.8~100.2	10.7	78.5~98.5	10.4	92.9~99.6	2.1	80.9~100.6	9.4
	0.2	79.8~95.6	6.2	79.8~95.6	6.2	76.7~100.8	8.9	86.3~107.1	7.8	84.4~100.3	5.8	86.3~107.1	7.4
	1.0	88.9~101.2	4.7	87.6~101.2	5.0	87.4~98.4	4.7	89.6~104.8	5.5	89.6~104.8	5.5	89.6~100.6	5.0
Ho	0.1	73.8~94.8	9.5	75.6~100.2	10.1	75.6~93.8	5.2	78.4~99.5	10.0	78.4~99.5	9.1	78.9~99.7	11.3
	0.2	76.8~97.5	6.9	76.8~100.3	10.0	81.6~102.0	5.8	78.9~103.2	8.1	74.5~102.0	8.6	78.4~94.9	7.1
	1.0	84.6~103.2	2.9	84.6~100.4	6.7	82.6~101.9	4.8	89.6~104.8	6.3	81.4~99.7	7.2	80.1~104.8	8.1
Er	0.1	73.8~97.4	10.0	73.8~91.3	7.3	73.8~90.2	6.4	73.8~98.5	10.9	74.5~102.0	10.5	78.4~98.5	9.7
	0.2	78.9~106.4	6.2	78.9~102.3	6.2	80.6~100.2	8.1	86.4~107.1	8.8	85.2~107.1	8.7	74.5~107.1	11.8
	1.0	88.9~102.3	4.6	82.1~102.3	7.8	84.2~102.1	6.9	89.5~100.6	4.5	84.5~98.0	4.3	86.4~105.6	6.6
Tm	0.1	72.3~98.5	9.5	72.3~100.5	10.2	79.5~100.1	8.1	74.5~102.0	10.9	75.9~97.9	8.1	74.5~102.0	11.9
	0.2	78.9~100.6	8.5	79.8~98.4	7.3	83.2~94.6	5.6	78.9~103.2	9.2	74.5~102.0	9.6	78.9~98.5	8.7
	1.0	86.4~103.2	6.4	88.6~100.2	3.7	88.6~100.2	3.7	86.4~101.7	6.4	86.3~101.7	6.1	84.5~101.7	6.5
Sc	0.2	73.8~94.6	9.7	73.8~93.8	8.1	75.8~94.6	8.4	78.5~99.5	9.1	86.3~104.8	6.4	77.5~99.5	9.7
	0.4	78.9~105.6	8.9	80.2~99.6	7.1	79.8~92.3	5.5	86.3~107.1	8.0	86.3~107.1	7.5	84.5~107.1	8.4
	2.0	88.9~102.3	5.6	87.7~99.7	5.2	84.6~100.5	3.2	87.8~104.8	5.8	89.6~104.8	5.7	90.6~104.8	5.0
Yb	0.1	74.8~99.5	9.5	78.5~90.1	1.7	78.5~97.8	8.3	80.1~100.6	7.3	75.9~98.3	8.1	86.3~100.6	6.7
	0.2	79.8~103.2	9.2	81.4~100.2	4.0	80.9~98.4	7.0	75.9~100.6	9.6	89.6~99.4	4.6	86.3~99.4	5.4
	1.0	85.2~105.6	7.7	85.2~98.5	4.3	83.8~98.6	6.4	89.6~101.7	4.6	89.6~96.8	2.5	86.3~97.9	4.3