



中华人民共和国出入境检验检疫行业标准

SN/T 2006—2007

进出口果汁中铅、镉、砷、汞检测方法 原子荧光光谱法

Determination of lead, cadmium, arsenic, mercury in fruit juice for import and export—Atomic fluorescence spectrometric method

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中 华 人 民 共 和 国 发 布
国家质量监督检验检疫总局

前 言

本标准的附录 A 为资料性附录。

本标准由国家认证认可监督管理委员会提出并归口。

本标准由中华人民共和国陕西出入境检验检疫局负责起草。

本标准主要起草人：乐爱山、张新智、赵收创、王昌钊。

本标准系首次发布的出入境检验检疫行业标准。

进出口果汁中铅、镉、砷、汞检测方法

原子荧光光谱法

1 范围

本标准规定了果汁中铅、镉、砷、汞的原子荧光光谱检测方法。

本标准适用于果汁中铅、镉、砷、汞的检测。

2 规范性引用文件

下列文件中的条款通过本标准的引用而成为本标准的条款。凡是注日期的引用文件,其随后所有的修改单(不包括勘误的内容)或修订版均不适用于本标准,然而,鼓励根据本标准达成协议的各方研究是否可使用这些文件的最新版本。凡是不注日期的引用文件,其最新版本适用于本标准。

GB/T 6682—1992 分析实验室用水规格和试验方法(neq ISO 3696)

3 方法提要

试样消解后,在特定介质中铅、砷与硼氢化钾反应生成挥发性氢化物,汞与硼氢化钾反应生成原子态汞,镉与硼氢化钾反应生成镉的挥发性物质,由氩气载入石英原子化器中,在空心阴极灯照射下,发射出特征波长的荧光,其荧光强度与测定元素含量成正比,与标准系列比较定量。

4 试剂和材料

除另有规定外,所用试剂均为分析纯,水为去离子水(符合 GB/T 6682—1992 中 4.2 条二级水的规定)。

4.1 硝酸:优级纯。

4.2 盐酸:优级纯。

4.3 抗坏血酸。

4.4 氢氧化钾。

4.5 铁氰化钾。

4.6 硫脲。

4.7 硼氢化钾。

4.8 硝酸溶液(1+99)V/V。

4.9 硝酸溶液(2+98)V/V。

4.10 盐酸溶液(2+98)V/V。

4.11 盐酸溶液(5+95)V/V。

4.12 抗坏血酸溶液(50 g/L):称取 5.0 g 抗坏血酸(4.3),溶于水中,稀释至 100 mL,混匀,用时现配。

4.13 氢氧化钾(10 g/L):称取 10.0 g 氢氧化钾(4.4),溶于水中,稀释至 1 000 mL,混匀。

4.14 氢氧化钾(5 g/L):称取 5.0 g 氢氧化钾(4.4)溶于水中,稀释至 1 000 mL,混匀。

4.15 硫脲溶液(50 g/L):称取 5.0 g 硫脲(4.6),溶于 100 mL 水中,混匀,用时现配。

4.16 硼氢化钾(10 g/L)混合溶液:称取 10.0 g 硼氢化钾(4.7),10.0 g 铁氰化钾(4.5),溶于氢氧化钾(4.13)中,稀释至 1 000 mL,混匀,用时现配。

4.17 硼氢化钾(30 g/L)混合溶液:称取 30.0 g 硼氢化钾(4.7),溶于氢氧化钾(4.14)中,稀释至

1 000 mL 混匀,用时现配。

4.18 硼氢化钾(10 g/L)混合溶液:称取 10.0 g 硼氢化钾(4.7),溶于氢氧化钾(4.14)中,稀释至 1 000 mL 混匀,用时现配。

4.19 预还原剂溶液:称取 5.0 g 硫脲(4.6)、5.0 g 抗坏血酸(4.3)溶于水中,稀释至 100 mL,用时现配。

4.20 铅标准储备液(1 mg/mL):GBW 08619。

4.21 镉标准储备液(1 mg/mL):GBW 08612。

4.22 砷标准储备液(1 mg/mL):GBW 08611。

4.23 汞标准储备液(1 mg/mL):GBW 08617。

4.24 钴标准储备液(1 mg/mL):GBW 08613。

4.25 铅标准工作液(50 $\mu\text{g/L}$):用硝酸溶液(4.8)逐级稀释铅标准储备液(4.20)。

4.26 镉标准工作液(6 $\mu\text{g/L}$):用盐酸溶液(4.10)逐级稀释镉标准储备液(4.21),加入 10 mL 硫脲溶液(4.15),1 mL 含钴溶液(4.29),用盐酸溶液(4.10)定容至 50 mL。用时现配。

4.27 砷标准工作液(50 $\mu\text{g/L}$):用盐酸溶液(4.11)逐级稀释砷标准储备液(4.22),加入预还原剂溶液(4.19)10 mL,用盐酸溶液(4.11)定容至 50 mL。用时现配。

4.28 汞标准工作液(10 $\mu\text{g/L}$):用硝酸溶液(4.9)逐级稀释汞标准储备液(4.23),用时现配。

4.29 含钴溶液(50 $\mu\text{g/mL}$):用硝酸溶液(4.8)逐级稀释钴标准储备液(4.24)。

5 仪器

5.1 原子荧光光度计:配备铅、镉、砷、汞空心阴极灯。

5.2 微波消解装置。

6 样品制备和保存

振荡果汁,使其充分混匀,均分为两份,分别置于洁净容器中,密封加贴样品标识,于 0℃~5℃ 条件下保存。制样操作过程中应防止样品受到污染或待测物含量的变化。

7 分析步骤

7.1 试样消解及待测溶液的制备

称取试样 0.5 g(精确至 0.001 g),置于消解罐中,加入 5 mL 水和硝酸 5 mL(4.1),按仪器操作规程设定温度压力,消化至消化液呈无色或淡黄色(微波消解装置工作条件参见附录 A 表 A.1)。同时做试剂空白实验。

7.1.1 测定铅时,样品消解完毕,赶尽硝酸,转移至 25 mL 容量瓶,用硝酸溶液(4.8)定容混匀,待测。

7.1.2 测定镉时,样品消解完毕,赶尽硝酸,转移至 25 mL 容量瓶,加入硫脲溶液(4.15)5 mL,0.5 mL 含钴溶液(4.29),用盐酸溶液(4.10)定容至刻度,混匀,待测。

7.1.3 测定砷时,样品消解完毕,赶尽硝酸,转移至 25 mL 容量瓶,加入预还原剂(4.19)2.5 mL,用盐酸溶液(4.11)定容至刻度,混匀,放置 30 min 待测。

7.1.4 测定汞时,样品消解完毕,转移至 25 mL 容量瓶,用硝酸溶液(4.9)定容至刻度,摇匀待测。

7.2 测定

7.2.1 根据使用仪器的类型及待测元素,将仪器调至最佳测定条件。设定标准系列各点浓度及试样质量(g)、定容体积(mL)、结果浓度单位。待仪器稳定后依次测定标准空白溶液、标准系列、样品空白溶液、样品溶液。

7.2.2 各元素标准系列浓度见表 1。

表 1 各元素标准系列浓度

元 素	S1/(μg/L)	S2/(μg/L)	S3/(μg/L)	S4/(μg/L)	S5/(μg/L)
Pb	2.00	5.00	10.00	20.00	50.00
Cd	0.50	1.00	2.00	4.00	6.00
As	2.00	5.00	10.00	20.00	50.00
Hg	1.00	2.00	4.00	8.00	10.00

7.2.3 各元素载流溶液见表 2。

表 2 各元素载流溶液

元 素	载流溶液
Pb	硝酸溶液(4.8)
Cd	盐酸溶液(4.10)
As	盐酸溶液(4.11)
Hg	硝酸溶液(4.9)

7.2.4 各元素还原剂溶液见表 3。

表 3 各元素还原剂溶液

元 素	还原剂溶液
Pb	硼氢化钾(10 g/L)混合溶液(4.16)
Cd	硼氢化钾(30 g/L)混合溶液(4.17)
As	硼氢化钾(10 g/L)混合溶液(4.18)
Hg	硼氢化钾(10 g/L)混合溶液(4.18)

7.2.5 原子荧光光谱仪工作条件参见附录 A 表 A.2。

7.2.6 标准曲线线性范围:铅 0 μg/L~50 μg/L、镉 0 μg/L~6 μg/L、砷 0 μg/L~50 μg/L、汞 0 μg/L~10 μg/L。

7.2.7 工作曲线:线性相关系数 r 大于等于 0.999。

8 结果计算

样品中测定元素的含量按式(1)计算

$$X = \frac{(c_1 - c_2) \times V}{m} \dots\dots\dots (1)$$

式中:

- X ——试样中测定元素的含量,单位为微克每千克(μg/kg);
- c_1 ——试样液中测定元素的浓度,单位为微克每升(μg/L);
- c_2 ——样品空白液中测定元素的浓度,单位为微克每升(μg/L);
- V ——试样液定容体积,单位为毫升(mL);
- m ——试样质量,单位为克(g)。

9 方法的测定低限、回收率

- 9.1 方法的测定低限:铅 25 μg/kg、镉 2 μg/kg、砷 10 μg/kg、汞 1 μg/kg。
- 9.2 方法回收率:在果汁中铅、镉、砷、汞的添加浓度及其回收率实验数据见表 4。

表 4 各元素添加浓度及回收率

元 素	添加量/($\mu\text{g}/\text{kg}$)	回收率/%
铅	25.00	89.6~110.0
	50.00	82.2~109.8
	100.00	90.2~102.5
	200.00	95.3~102.0
镉	2.00	75.0~80.0
	10.00	80.0~95.6
	20.00	85.2~105.0
	40.00	93.4~107.5
砷	10.00	86.0~110.0
	50.00	88.0~106.2
	100.00	96.3~108.6
	200.00	98.0~105.3
汞	1.00	70.0~89.0
	5.00	77.6~96.0
	10.00	90.8~106.8
	20.00	96.3~110.0

附 录 A
(资料性附录)

原子荧光光谱仪及微波消解装置工作条件

表 A.1 微波消解装置工作条件

步 骤	功率/W		升温时间/ min	压力/ MPa	控制温度/ ℃	保持时间/ min
	最 大	%				
1	300	100	6	5.52	120	5
2	300	100	8	5.52	175	10

表 A.2 原子荧光光谱仪工作条件

负高压 PMT/V	Pb:240 As:270	Cd:240 Hg:240	加热温度/℃	200
灯电流/mA	Pb:40 As:60	Cd:40 Hg:15	载气流量/(mL/min)	600
辅助灯电流/mA	Pb:20 As:20	Cd:20 Hg:0	屏蔽气流量/(mL/min)	800
观测高度/mm	8		测量方法	Std. Curve
读数方式	Peak. Area		读数时间/s	8
延迟时间/s	1.5		重复次数	3

Foreword

Annex A of the standard is an informative annex.

The standard was proposed and under the jurisdiction of the National Regulation Commission for Certification and Accreditation.

The standard was drafted by Shaanxi Entry-Exit Inspection and Quarantine Bureau.

This standard was mainly drafted by Yue Aishan, Zhang Xinzhi, Zhao Shouchuang, and Wang Changzhao.

The standard is a professional standard for entry-exit inspection and quarantine promulgated for the first time.

Note: This English version, a translation from the Chinese text, is only for reference.

Determination of lead, cadmium, arsenic, mercury in fruit juice for import and export—Atomic fluorescence spectrometric method

1 Scope

The Standard specifies methods for the determination of lead, cadmium, arsenic, and mercury in fruit juice with the atomic fluorescence spectrometric method.

The Standard is applicable to the determination of lead, cadmium, arsenic, and mercury in fruit juice.

2 Document Quoted for Standard

The following normative documents contain provisions which, through reference in this text, constitute provisions of this Professional Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based in this Professional 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—1992 Water for analytical laboratory use—Specification and test methods (neq ISO 3696)

3 Method abstract

After the sample is cleared up with nitric acid in microwave devices, lead, cadmium, arsenic, and mercury contained in it. After reaction with potassium borohydride, lead and arsenic introduce volatile hydride, mercury introduces Hg vapour, and cadmium introduces volatile matter of cadmium. These products are carried into quartz atomizer through argon gas respectively. Under the irradiation of specially configured hollow cathode lamp, it emits fluorescence with characteristic wavelength. The fluorescence intensity is directly proportional to the content of elements determined, and quantified after the comparison with standard series.

4 Reagent and Solution

Unless indicated, all reagents used in the Standard are of analytical grade, and water used in experiments is deionized water (Conforms to Grade 2 in the Article 4.2 of GB/T 6682—1992).

- 4.1 Nitric acid (GR).
- 4.2 Hydrochloric acid (GR).
- 4.3 Ascorbic acid.
- 4.4 Potassium hydroxide.
- 4.5 Potassium ferricyanide.
- 4.6 Thiourea.
- 4.7 Potassium borohydride.
- 4.8 Nitric acid solution (1 + 99) V/V.
- 4.9 Nitric acid solution (2 + 98) V/V.
- 4.10 Hydrochloric acid solution (2 + 98) V/V.
- 4.11 Hydrochloric acid solution (5 + 95) V/V.
- 4.12 Ascorbic acid solution (50 g/L): Dissolve 5.0 g of ascorbic acid (4.3) in 100 mL water and it should be prepared daily.
- 4.13 Potassium hydroxide (10 g/L): Dissolve 10.0 g of potassium hydroxide (4.4) in 1 000 mL water.
- 4.14 Potassium hydroxide (5 g/L): Dissolve 5.0 g of potassium hydroxide (4.4) in 1 000 mL water.
- 4.15 Thiourea solution (50 g/L): Dissolve 5.0 g of thiourea (4.6) in 100 mL water and it should be prepared daily.
- 4.16 Mixed solution of potassium borohydride (10 g/L): Dissolve 10.0 g of potassium borohydride (4.7) and 10.0 g of potassium ferricyanide (4.5) in potassium hydroxide (4.13), dilute to 1 000 mL and it should be prepared daily.
- 4.17 Mixed solution of potassium borohydride (30 g/L): Dissolve 30.0 g of potassium borohydride (4.7) in potassium hydroxide (4.14), dilute to 1 000 mL and it should be prepared daily.
- 4.18 Mixed solution of potassium borohydride (10 g/L): Dissolve 10.0 g of potassium borohydride (4.7) in potassium hydroxide (4.14), dilute to 1 000 mL and it should be prepared daily.

- 4.19 Reducing agent solution: Dissolve 5.0 g of thiourea (4.6) and 5.0 g of ascorbic acid (4.3) in water, and dilute to 100 mL with water and it should be prepared daily.
- 4.20 Lead standard stock solution (1 mg/mL): GBW 08619.
- 4.21 Cadmium standard stock solution (1 mg/mL): GBW 08612.
- 4.22 Arsenic standard stock solution (1 mg/mL): GBW 08611.
- 4.23 Mercury standard stock solution (1 mg/mL): GBW 08617.
- 4.24 Cobalt standard stock solution (1 mg/mL): GBW 08613.
- 4.25 Lead standard working solution (50 $\mu\text{g/L}$): Using nitric acid solution (4.8) to gradually dilute lead standard stock solution (4.20).
- 4.26 Cadmium standard working solution (6 $\mu\text{g/L}$): Gradually diluting cadmium standard stock solution (4.21), add 10 mL of thiourea solution (4.15), 1 mL of cobalt solution (4.29), and hydrochloric acid (4.10) is added to 50 mL.
- 4.27 Arsenic standard working solution (50 $\mu\text{g/L}$): Gradually diluting arsenic standard stock solution (4.22). 10 mL of reducing agent solution (4.19) is added, and Hydrochloric acid (4.11) is added to 50 mL.
- 4.28 Mercury standard working solution (10 $\mu\text{g/L}$): Using nitric acid (4.9) to gradually dilute mercury standard stock solution (4.23).
- 4.29 Cobalt solution (50 $\mu\text{g/mL}$): Using nitric acid (4.8) gradually diluting cobalt standard stock solution (4.24) to the thickness of 50 $\mu\text{g/mL}$.

5 Apparatus

- 5.1 Atomic Fluorescence Spectrophotometer equipped with lead, cadmium, arsenic, and mercury hollow cathode lamps.
- 5.2 Microwave digestion devices.

6 Sample preparation and storage

Rock the fruit juice and mix evenly, then divide it into two parts and the test sample should be sealed, labelled and stored in $0^{\circ}\text{C} \sim 5^{\circ}\text{C}$. Protect samples from contamination and prevent the change of the content of elements determined in the process of preparation.

7 Analyzing Procedure

7.1 Sample Digestion & Preparation for Solution Determined

Weigh 0.5 g of sample (with an accuracy of 0.001 g) and add 5 mL of water and 5 mL of nitric acid (4.1) into digestion jar; set the temperature and pressure according to instrument operation rules until digestion solution becomes colorless or light yellow (working conditions of microwave digestion devices; See appendix A table A.1). Blank test shall be carried out in parallel with the analysis of the test samples under the same conditions.

7.1.1 Determinating the sample of lead: completing the digestion, removing nitric acid, using nitric acid solution (4.8) to transfer and place into a 25 mL volumetric flask. Mixing evenly and awaiting determination.

7.1.2 Determinating the sample of cadmium: completing digestion, removing nitric acid and transferring to a 25 mL volumetric flask, adding 5 mL of thiourea (4.15), 0.5 mL of cobalt solution (4.29), and hydrochloric acid (4.10) to the scale. Mixing evenly and awaiting determination.

7.1.3 Determinating the sample of arsenic: completing digestion, removing nitric acid transfer to a 25 mL volumetric flask, adding 2.5 mL of reducing agent (4.19), and hydrochloric acid (4.11) to the scale. Mixing evenly and putting aside 30 min for determination.

7.1.4 Determinating the sample of mercury: completing digestion, transfer to a 25 mL volumetric flask, add nitric acid (4.9) to the scale. Mixing evenly and awaiting determination.

7.2 Determination

7.2.1 Instruments are adjusted to the optimum condition in accordance with the categories and elements awaiting determination, concentration of each point, sample weight (g), vessel volume (mL), dilution rate, and result concentration unit are designed. After instruments become stable, determination will be carried out in the order of standard blank solution, standard series, sample blank solution, and sample solution.

7.2.2 Standard Series of each element see table 1.

Table 1—Standard Series of each element

Elements	S1/(μ g/L)	S2/(μ g/L)	S3/(μ g/L)	S4/(μ g/L)	S5/(μ g/L)
Pb	2.00	5.00	10.00	20.00	50.00
Cd	0.50	1.00	2.00	4.00	6.00
As	2.00	5.00	10.00	20.00	50.00
Hg	1.00	2.00	4.00	8.00	10.00

7.2.3 Current-carrying solution of each element see table 2.

Table 2—Current-carrying solution of each element

Elements	Current-carrying solution
Pb	HNO ₃ (4. 8)
Cd	HCl(4. 10)
As	HCl(4. 11)
Hg	HNO ₃ (4. 9)

7.2.4 Reducer solution of each element see table 3.

Table 3—Reducer solution of each element

Elements	Reducer solution
Pb	Mixed solution of potassium borohydride(10 g/L) (4. 16)
Cd	Mixed solution of potassium borohydride(30 g/L) (4. 17)
As	Mixed solution of potassium borohydride(10 g/L) (4. 18)
Hg	Mixed solution of potassium borohydride(10 g/L) (4. 18)

7.2.5 Working condition of atomic fluorescence spectroscopy see appendix A Table A. 2.

7.2.6 Linear scope of standard curve: Lead 0 μg/L~50 μg/L, cadmium 0 μg/L~6 μg/L, arsenic 0 μg/L~50 μg/L, and mercury 0 μg/L~10 μg/L.

7.2.7 Working curve: The coefficient of working curve $r \geq 0.999$.

8 Result calculation

Content of elements in the sample are determined by formula(1):

$$X = \frac{(c_1 - c_2) \times V}{m} \dots\dots\dots (1)$$

where

X—Content of elements in the sample, μg/kg;

c₁—Concentration of elements in the sample, μg/L;

c_2 —Concentration of elements in the blank solution of sample, $\mu\text{g/L}$;

V —Volume of sample, mL;

m —Sample weight, g;

9 dedection limits and recovery

9.1 Dedection limits: Lead 25 $\mu\text{g/kg}$, cadmium 2 $\mu\text{g/kg}$, arsenic 10 $\mu\text{g/kg}$, and mercury 1 $\mu\text{g/kg}$.

9.2 Recovery: experiment data of supplementation concentration and recovery of lead, cadmium, arsenic, and mercury in fruit juice see table 4.

Table 4—Supplementation concentration and recovery rate of each element

Element	supplementation/($\mu\text{g/kg}$)	recovery rate/%
Pb	25.00	89.6~110.0
	50.00	82.2~109.8
	100.00	90.2~102.5
	200.00	95.3~102.0
Cd	2.00	75.0~80.0
	10.00	80.0~95.6
	20.00	85.2~105.0
	40.00	93.4~107.5
As	10.00	86.0~110.0
	50.00	88.0~106.2
	100.00	96.3~108.6
	200.00	98.0~105.3
Hg	1.00	70.0~89.0
	5.00	77.6~96.0
	10.00	90.8~106.8
	20.00	96.3~110.0

Annex A
(Informative)

Working Condition of Atomic Fluorescence Spectroscopy and Microwave Digestion Device

Table A. 1—Working Condition of Microwave Digestion Device (American CEM MARS5 Series)

Procedure	Power/W		Heating Time/min	Pressure/MPa	Controlled Temperature/℃	Maintained Time/min
	Maximum	%				
1	300	100	6	5.52	120	5
2	300	100	8	5.52	175	10

Table A. 2—Working Condition of Atomic Fluorescence Spectroscopy(Beijing Jitian AFS-930 Series)

Negative High Pressure PMT/V	Pb:240 As:270	Cd:240 Hg:240	Heating Temperature/℃	200
Lamp Current/mA	Pb:40 As:60	Cd:40 Hg:15	Flow of Carrier Gas(mL/min)	600
Auxiliary Lamp Current/mA	Pb:20 As:20	Cd:20 Hg:0	Flow of Shield Gas/(mL/min)	800
Observed Altitude/mm	8		Observation Method	Std. Curve
Reading Way	Peak. Area		Reading Time/s	8
Delay Time/s	1.5		Repeated Times	3

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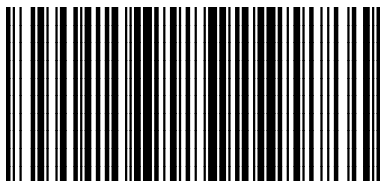
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