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中华人民共和国出入境检验检疫行业标准

SN/T 3927—2014

出口乳制品中硫氰酸钠含量的测定

Determination of sodium thiocyanate in dairy products for export

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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：中华人民共和国山东出入境检验检疫局、中华人民共和国山西出入境检验检疫局、湖南省检验检疫科学技术研究院。

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出口乳制品中硫氰酸钠含量的测定

1 范围

本标准规定了出口乳制品中硫氰酸钠含量的离子色谱测定方法和气相色谱测定方法。

本标准适用于灭菌乳、杀菌乳、酸牛乳、配方乳、乳饮料、乳粉、配方乳粉、干酪、炼乳等乳制品中硫氰酸钠含量的测定。

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 6682 分析实验室用水规格和试验方法

第一法 离子色谱法

3 原理

试样中硫氰酸根经乙腈提取、沉淀蛋白后，对提取液进行净化，以氢氧化钾溶液为淋洗液，阴离子交换柱分离，电导检测器检测。以保留时间定性，外标法定量。

4 试剂和材料

除另有规定外，所用试剂均为分析纯，试验用水符合 GB/T 6682 中一级水的规定。

4.1 硫氰酸钠标准物质(sodium thiocyanate，分子式：NaSCN，CAS 编号：540-72-7)：纯度≥99.99%。

4.2 乙腈(CH_3CN)：色谱纯。

4.3 甲醇(CH_3OH)：色谱纯。

4.4 硫氰酸钠(以硫氰酸根计)标准储备液(1 000 mg/L)：准确称取 0.139 7 g 硫氰酸钠，用水定容至 100 mL。在 0 ℃～4 ℃冰箱中保存，有效期为 6 个月。

4.5 硫氰酸钠(以硫氰酸根计)标准中间液(10 mg/L)：准确移取硫氰酸钠标准储备液(4.4)1.00 mL 于 100 mL 容量瓶中，用水稀释至刻度，摇匀。在 0 ℃～4 ℃冰箱中保存，有效期为 1 个月。

4.6 尼龙滤膜：0.22 μm。

4.7 RP 柱(1.0 mL)，或性能相当的能去除有机物质的前处理小柱，使用前依次用 5 mL 甲醇、10 mL 水活化，放置 30 min 后使用。

5 仪器和设备

5.1 离子色谱仪：配电导检测器。

5.2 离心机：转速不低于 6 000 r/min。

5.3 涡旋混匀器。

5.4 分析天平：感量 0.1 mg、0.01 g。

5.5 离心管：15 mL。

6 试样制备与保存

从所有样品中取出有代表性样品约 500 g 或 500 mL，将样品充分混匀，均分成两份，分别装入洁净容器中，密封，并标明标记，于 0 ℃～4 ℃条件下保存。

7 分析步骤

7.1 试样处理

7.1.1 灭菌乳等液体样品：称取 4 g(精确至 0.01 g)样品，用乙腈(4.2)定容至 10 mL(V_1)，转移至离心管中，涡旋混匀 2 min，室温静置沉降蛋白 20 min，以 6 000 r/min 转速离心 10 min。准确移取上层清液 1.00 mL(V_2)，用水定容至 10 mL(V_3)并混匀。取上述溶液适量，依次过 0.22 μm 尼龙滤膜、RP 柱或性能相当者，弃去前 3 mL 滤液，收集后面滤液供离子色谱仪测定。可根据样品中硫氰酸根含量情况，用水适当稀释待测样品溶液。

7.1.2 乳粉等固体样品：称取 1 g(精确至 0.01 g)样品，加入 4 g 水，立即摇匀，涡旋混匀 2 min，用乙腈(4.2)定容至 10 mL(V_1)，混匀后转移至离心管中，室温静置沉降蛋白 20 min，以 6 000 r/min 转速离心 10 min。准确移取上层清液 1.00 mL(V_2)，用水定容至 10 mL(V_3)并混匀。取上述溶液适量，依次过 0.22 μm尼龙滤膜、RP 柱或性能相当者，弃去前 3 mL 滤液，收集后面滤液供离子色谱仪测定。可根据样品中硫氰酸根含量情况，用水适当稀释待测样品溶液。

7.2 色谱分析参考条件

7.2.1 色谱柱：氢氧化物选择性、疏水性低且可兼容梯度洗脱的高容量阴离子交换柱，如 Ion Pac® AS 16 型分析柱，4 mm×250 mm(配备 Ion Pac® AG 16 型保护柱 4 mm×50 mm)，或性能相当的离子色谱柱。

7.2.2 柱温箱温度：30 ℃。

7.2.3 淋洗液：氢氧化钾溶液，浓度为 45 mmol/L～60 mmol/L，梯度淋洗，淋洗液 OH^- 浓度见表 1。

表 1 淋洗液 OH^- 浓度表

时间 min	流速 mL/min	OH^- 浓度 mmoL/L
0.00～13.00	1.00	45.0
13.00～18.00	1.00	60.0
18.00～23.00	1.00	45.0

7.2.4 抑制器：ASRS-300 4 mm 阴离子抑制器，或选用其他具有相同功能的抑制器；外加水抑制模式，抑制电流 112 mA～149 mA，外加水流量 1.5 mL/min。

7.2.5 淋洗液流速：1.0 mL/min。

7.2.6 进样体积：100 μL。

7.2.7 检测器：电导检测器。

7.3 绘制标准曲线

取硫氰酸钠标准中间液(4.5),根据需要用水稀释制取系列标准工作溶液(参考线性范围为0.01 mg/L～1.00 mg/L),按色谱分析条件(7.2),由低到高浓度依次进样测定。根据所得色谱图,以硫氰酸钠(以硫氰酸根计)的浓度为横坐标、以峰面积(或峰高)响应值为纵坐标,绘制标准曲线,并计算线性回归方程。典型离子色谱图参见附录A中的图A.1。

7.4 样品分析

将测试溶液按色谱分析条件(7.2)进行测定,记录色谱图。根据硫氰酸根保留时间定性,测量测试溶液中的硫氰酸根的峰面积(或峰高)响应值,采用外标法定量。测试溶液中硫氰酸根的响应值应在标准线性范围内。

7.5 空白试验

除不称取试样外,其余均按上述步骤进行。

8 结果计算

试样中硫氰酸钠(以硫氰酸根计)的含量按式(1)计算:

$$X=\frac{(c-c_0)\times V_1\times V_3\times 1\,000}{m\times V_2\times 1\,000} \qquad \cdots\cdots(1)$$

式中:

X ——试样中硫氰酸钠(以硫氰酸根计)的含量,单位为毫克每千克(mg/kg);

c ——测试溶液中硫氰酸钠(以硫氰酸根计)的浓度,单位为毫克每升(mg/L);

c_0 ——空白溶液中硫氰酸钠(以硫氰酸根计)的浓度,单位为毫克每升(mg/L);

V_1 ——样品用乙腈提取时定容体积,单位为毫升(mL);

V_3 ——提取液用水稀释时定容体积,单位为毫升(mL);

m ——试样质量,单位为克(g);

V_2 ——用水稀释时移取提取液的体积,单位为毫升(mL)。

计算结果保留至小数点后两位。

9 测定低限

本方法对乳制品中硫氰酸钠(以硫氰酸根计)含量的测定,灭菌乳等液态样品测定低限为0.25 mg/kg,乳粉等固态样品测定低限为1.00 mg/kg。

10 回收率与精密度

样品添加回收率及精密度试验数据参见附录B中的表B.1。

第二法 气相色谱法

11 原理

试样中硫氰酸根经水提取后,加入氯胺T将硫氰酸根转变为氯化氰,顶空进样,气相色谱法检测,

外标法定量。

12 试剂和材料

除另有规定外，所用试剂均为分析纯，试验用水符合 GB/T 6682 中一级水的规定。

12.1 硫氰酸钠标准品(sodium thiocyanate，分子式：NaSCN，CAS 编号：540-72-7)：纯度≥99.99%。

12.2 乙酸锌。

12.3 氯胺 T：保存于干燥器中。

12.4 乙酸锌溶液：称取 22 g 乙酸锌(12.2)，溶于水中，并稀释定容于 100 mL。

12.5 氯胺 T 溶液：称取 1 g 氯胺 T(12.3)，溶于水中，并稀释定容于 100 mL。

12.6 硫氰酸钠(以硫氰酸根计)标准储备溶液(1 000 mg/L)：准确称取 0.139 7g 硫氰酸钠，用水定容至 100 mL。在 0 ℃～4 ℃冰箱中保存，有效期 6 个月。

12.7 硫氰酸钠(以硫氰酸根计)标准中间溶液(10 mg/L)：准确移取 1.00 mL 的硫氰酸钠标准储备溶液(12.6)于 100 mL 的容量瓶，用水稀释至刻度。在 0 ℃～4 ℃冰箱中保存，有效期 1 个月。

12.8 硫氰酸钠(以硫氰酸根计)标准工作溶液：移取适量标准中间溶液(12.7)用水稀释为浓度 0、0.005、0.01、0.02、0.05、0.1 mg/L 的标准工作溶液。

13 仪器与设备

13.1 气相色谱：配电子捕获检测器(ECD)。

13.2 顶空进样器。

13.3 顶空瓶：20 mL。

13.4 涡旋混匀器。

13.5 分析天平：感量 0.000 1 g、0.01 g。

13.6 离心机：转速不低于 4 000 r/min。

14 试样制备与保存

从所有样品中取出有代表性样品约 500 g 或 500 mL，将样品充分混匀，均分成两份，分别装入洁净容器中，密封，并标明标记，于 0 ℃～4 ℃条件下保存。

15 测定步骤

15.1 试样处理

称取试样 1 g(精确至 0.01 g)，加入 4 mL 乙酸锌溶液(12.4)，用水定容至 100 mL，放置 1 h 后，以 4 000 r/min 转速离心 5 min。准确移取 10 mL 上清液于顶空瓶中，加入 0.1 mL 氯胺 T 溶液(12.5)，立即加盖密封，涡流混合，待测。

15.2 色谱分析参考条件

15.2.1 顶空分析条件参见附录 C。

15.2.2 气相色谱条件如下：

a) 色谱柱：BP10 毛细管柱，25 m×0.32 mm(内径)×0.50 μm(膜厚)，或性能相当者；

b) 色谱柱温度：40 ℃保持 5 min，以 50 ℃/min 速率升至 200 ℃保持 2 min；

c) 载气：氮气，纯度不低于 99.999%；
d) 进样口温度：150 ℃；
e) 检测器温度：260 ℃；
f) 分流比：100∶1；
g) 柱流速：1.0 mL/min。

15.3 标准曲线绘制

准确移取 10 mL 标准工作液(12.8)于顶空瓶中，分别加入 0.1 mL 氯胺 T 溶液，立即加盖密封，涡流混合，待测。按色谱分析条件(15.2)，由低到高浓度依次进样测定。根据所得色谱图，以硫氰酸钠(以硫氰酸根计)的浓度为横坐标、以峰面积(或峰高)响应值为纵坐标，绘制标准曲线，并计算线性回归方程。在上述色谱条件下，硫氰酸根离子衍生物的保留时间约为 2.50 min，典型色谱图参见附录 A 中的图 A.2。

15.4 样品分析

将测试溶液按色谱分析条件(15.2)进行测定，记录色谱图。根据硫氰酸根离子衍生物保留时间定性，测量测试溶液中硫氰酸根离子衍生物的峰面积(或峰高)响应值，采用外标法定量。测试溶液中硫氰酸根离子衍生物的响应值应在标准线性范围内。

15.5 空白试验

除不称取试样外，其余均按上述步骤进行。

15.6 结果计算和表述

试样中硫氰酸钠(以硫氰酸根计)的含量按式(2)计算：

$$X=\frac{(c-c_0)\times V\times 1\,000}{m\times 1\,000} \qquad \cdots\cdots(2)$$

式中：

X ——试样中硫氰酸钠(以硫氰酸根计)的含量，单位为毫克每千克(mg/kg)；

c ——测试溶液中硫氰酸钠(以硫氰酸根计)的浓度，单位为毫克每升(mg/L)；

c_0 ——空白溶液中硫氰酸钠(以硫氰酸根计)的浓度，单位为毫克每升(mg/L)；

V ——样液定容体积，单位为毫升(mL)；

m ——样品质量，单位为克(g)。

计算结果保留至小数点后一位。

16 测定低限

本方法对乳制品中硫氰酸钠(以硫氰酸根计)的测定低限为 1.0 mg/kg。

17 回收率与精密度

样品添加回收率及精密度实验数据参见附录 B 中的表 B.2。

附 录 A
（资料性附录）
标准溶液色谱图

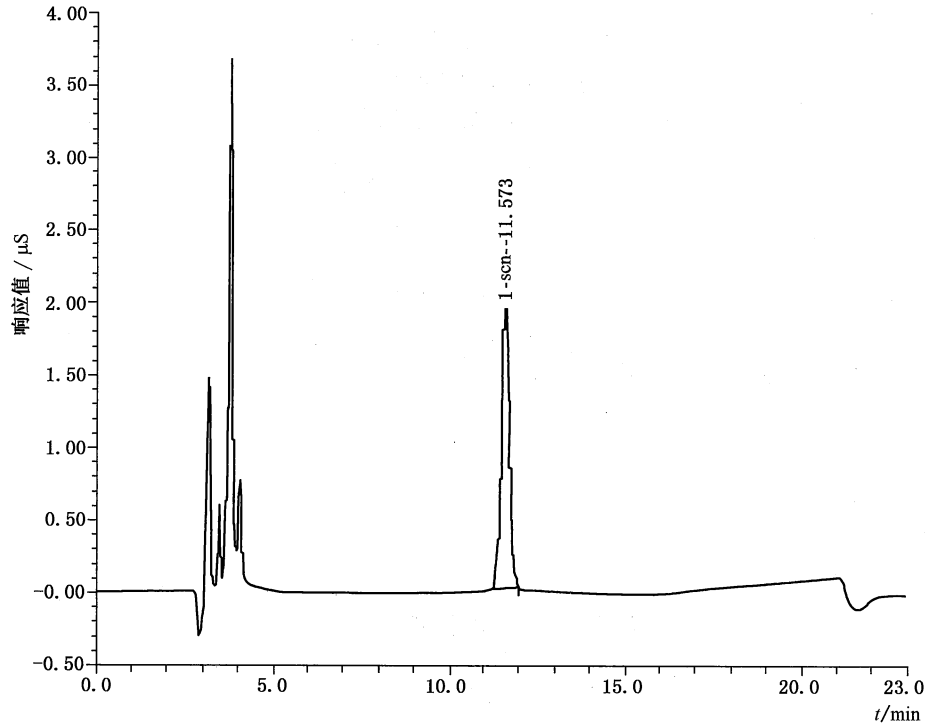

图 A.1 硫氰酸钠（以硫氰酸根计）标准溶液的离子色谱图（1 mg/L）

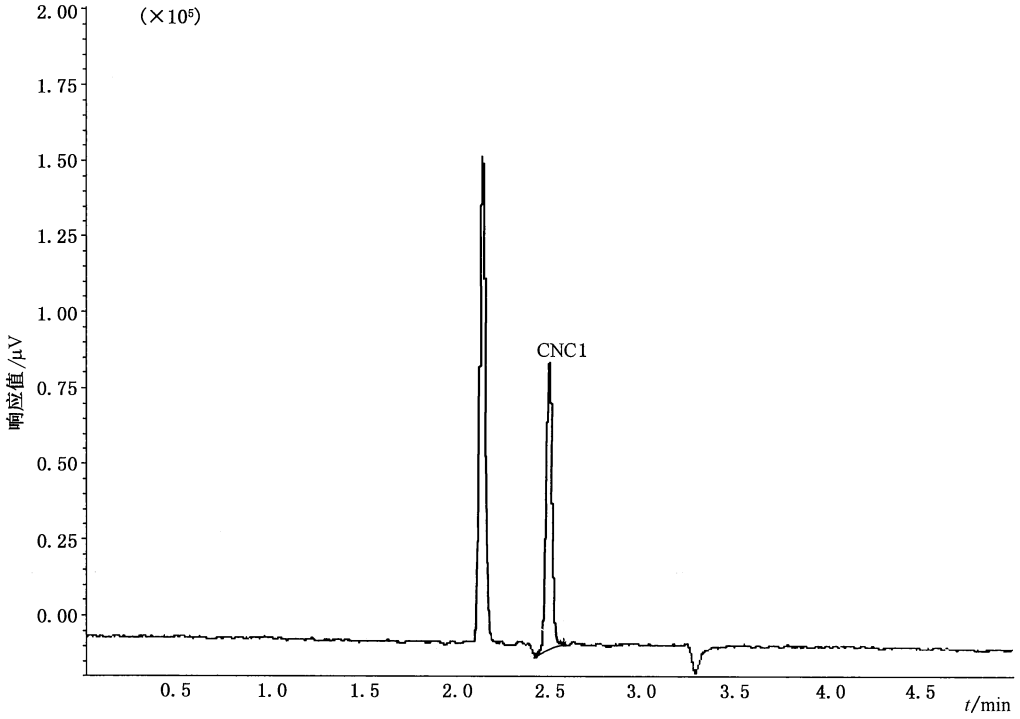

图 A.2　硫氰酸钠(以硫氰酸根计)离子衍生物的气相色谱图(0.01 mg/L)

附 录 B
（资料性附录）
样品添加回收率与精密度实验数据表

表 B.1 样品添加回收率与精密度实验数据表（离子色谱法）

样品名称	硫氰酸钠（以硫氰酸根计）添加浓度 mg/kg	回收率范围 %	相对标准偏差 %
灭菌乳	0.25	80.4～100.2	6.45
	0.50	92.3～104.1	4.89
	2.50	93.2～101.2	2.99
杀菌乳	0.25	88.6～105.5	6.31
	0.50	88.9～105.8	5.43
	2.50	90.6～103.8	4.61
酸牛乳	0.25	88.3～104.4	5.35
	0.50	92.8～106.0	4.83
	2.50	90.4～101.2	4.15
配方乳	0.25	87.5～105.1	7.78
	0.50	88.2～104.1	7.74
	2.50	90.8～104.4	4.74
乳饮料	0.25	86.1～108.7	8.36
	0.50	86.6～104.2	6.94
	2.50	91.6～102.8	3.70
乳粉	1.00	90.4～105.6	5.59
	2.00	91.3～103.3	4.84
	10.00	91.8～102.7	3.90
配方乳粉	1.00	91.7～104.3	4.73
	2.00	92.1～98.5	2.57
	10.00	92.1～103.7	3.95
干酪	1.00	90.9～102.6	4.31
	2.00	91.5～105.7	5.08
	10.00	95.2～104.5	3.31
炼乳	1.00	91.1～104.7	4.58
	2.00	93.1～105.5	4.24
	10.00	92.2～103.9	4.72

表 B.2　样品添加回收率与精密度实验数据表(气相色谱法)

样品名称	硫氰酸钠(以硫氰酸根计) 添加浓度 mg/kg	回收率范围 %	相对标准偏差 %
杀菌乳	1.0	94.0～110.0	5.36
	2.0	90.5～108.5	5.60
	10.0	90.2～107.3	7.49
酸牛乳	1.0	90.0～110.0	6.86
	2.0	90.5～108.5	6.78
	10.0	90.1～107.2	6.22
乳粉	1.0	91.0～109.0	6.86
	2.0	91.5～106.5	5.07
	10.0	90.4～109.1	7.39
乳饮料	1.0	91.0～110.0	7.53
	2.0	90.5～108.5	7.37
	10.0	93.1～109.3	4.98
干酪	1.0	93.0～110.0	5.47
	2.0	94.5～108.5	3.91
	10.0	90.2～109.3	7.89
配方乳	1.0	92.0～109.0	5.92
	2.0	93.5～110.0	6.30
	10.0	92.1～108.4	5.42

附 录 C
（资料性附录）
顶空进样分析条件[1)]

顶空分析条件如下：

a) 顶空平衡温度：35 ℃；
b) 取样针温度：110 ℃；
c) 传输线温度：120 ℃；
d) 顶空加热时间：20 min；
e) 进样时间：0.03 min；
f) 加压时间：2.5 min；
g) 载气：12.5 psi(1 psi=6.895 kPa)。

1) 非商业性声明：附录C所列的顶空进样分析条件是在PE TurboMatrix 16型顶空进样器上完成的，此处列出试验用仪器型号仅为提供参考，并不涉及商业目的，鼓励标准使用者尝试不同厂家或型号的仪器。

Foreword

The standard are compiled according as the GB/T 1.1—2009.

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

The standard was drafted by Shandong Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, Shanxi Entry-Exit Inspection and Quarantine Bureau of the People's Republic of China, Hunan Academy of Inspection and Quarantine.

The standard was mainly drafted by Hu Qiaoru, Yang Lijun, Wang Jing, Dulijun, Cui Fengjie, Song Xiaohua, Cong Weihong, Liu Yumin, Fu Yingwen, Cui He, Zhai Jinyi, Zhao Youyou, Liu Hongyan, Yao Yating, Huang zhiqiang.

Determination of sodium thiocyanate in dairy products for export

1 Scope

This standard specifies the ion chromatographic method and gas chromatographic method for the determination of sodium thiocyanate in dairy products of export.

This standard is applicable to the determination of sodium thiocyanate in sterilized milk, pasteurized milk, yoghurt, formula milk, milk beverage, milk powder, formula milk powder, cheese and condensed milk of export.

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 6682 Water for analytical laboratory use—Specification and test method

Ion chromatography

3 Principle

The sample was extracted and precipitated protein with acetonitrile, then the extract was cleaned, separated by anion exchange column, potassium hydroxide solution as eluent. The determination was aceieved by ion chromatography equipped with conductance detector, qualitatified with the retention time and quantified by external standard method.

4 Reagents and materials

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

4.1 Sodium thiocyanate standard (NaSCN, CAS No.: 540-72-7): purity≥99.99%.

4.2 Acetonitrile (CH_3CN): HPLC grade.

4.3 Methanol (CH_3OH): HPLC grade.

4.4 Sodium thiocyanate (SCN^-) standard storage solution (1 000 mg/L): accurately weigh sodium thiocyanate 0.139 7 g, then transfer it into 100 mL volumetric flask, dillute to mark with water. Preserve at 0 ℃～4 ℃ for six month.

4.5 Sodium thiocyanate (SCN^-) standard work solution (10 mg/L): according to need, accurately pipette sodium thiocyanate standard storage solution (4.4) 1.00 mL into 100 mL volumetric flask dillute to mark with water. Preserve at 0 ℃～4 ℃ for one month.

4.6 Organic needle filter membrane: 0.22 μm.

4.7 OnGuard Ⅱ RP column (1.0 mL): activation with 5 mL methanol, 10 mL water, standing for 30 min.

5 Apparatus and equipment

5.1 Ion chromatography: equipped with conductance detector.

5.2 Centrifuge: ≥6 000 r/min.

5.3 Vortex mixer.

5.4 Balance: with 0.01 g and 0.000 1 g sensivity.

5.5 Color comparison tube with cap: 15 mL.

6 Sample preparation and storage

Collect a 500 g or 500 mL sample that is representative of the entire sample. The sample should be mixed directly and divided into two equal portions. Each portion is placed into a clean vessel as a test sample, which is then sealed. All the samples should be stored under 0 ℃～4 ℃.

7 Analytical procedure

7.1 Sample pretreatment

7.1.1 Liquid Samples

Accurately weigh 4.0 g test sample (accurate to 0.01 g) into a color comparison tube with cap, dillute to 10 mL (V_1) with acetonitrile. Shake it on the vortex mixer for 2 min, stand for 20 min to precipi-

tate protein at room temperature and then centrifuge at 6 000 r/min for 10 min. Accurately pipette 1.0 mL (V_2) of the supernatant into a color comparison tube with cap, dillute to 10 mL (V_3) with water, shake it on the vortex mixer and take the extract to filter through a 0.22 μm membrane, then cleaned by SPE column(for example Guard Ⅱ RP column), discard the first 3 mL of solution and take the middle section of the filtrate for Ion chromatography determination. If the sodium thiocyanate exceeds the range of the standard curve, the sample amount should be reduced or the multiple should be increased.

7.1.2 Solid sample

Accurately weigh 1.0 g test sample (accurate to 0.01 g) into a color comparison tube with cap, add 4 g water and shake it on the vortex mixer for 2 min, then dillute to 10 mL(V_1)with acetonitrile. Mix it well on the vortex, then stand for 20 min to precipitate prettied at room temperature and then centrifuge at 6 000 r/min for 10 min. Accurately pipette 1.0 mL (V_2) of the supernatant into a color comparison tube with cap, dillute to 10 mL (V_3) with water, shake it on the vortex mixer and take the extract to filter through a 0.22 μm membrane, then cleaned by SPE column(for example Guard Ⅱ RP column), discard the first 3 mL of solution and take the middle section of the filtrate for Ion chromatography determination. If the sodium thiocyanate exceeds the range of the standard curve, the sample amount should be reduced or the multiple should be increased.

7.2 Chromatography operating conditions

7.2.1 Chromatography column: hydroxide selective, high-capacity anion exchange column compatible with gradient elution, for example Ion Pac® AS 16, 4 mm × 250 mm (with Ion Pac® AG 16, 4 mm × 50 mm guard column).

7.2.2 The temperature of column: 30 ℃.

7.2.3 Eluent: potassium hydroxide solution, the concentration of 45 mmol/L～60 mmol/L, utilizing a gradient elution program (0.00 min～13.00 min, 45.0 mmol/L; 13.00 min～18.00 min, 60.0 mmol/L; 18.00 min～23.00 min, 45.0 mmol/L).

7.2.4 Suppressor: ASRS-300 4 mm anion suppressor; external water suppression mode (flow rate: 1.5 mL/min), suppression current is 112 mA～149 mA.

7.2.5 Flow rate: 1.0 mL/min.

7.2.6 Injection volume: 100 μL.

7.2.7 Detector: conductance detector.

7.3 Standard curve

According to need, dilute sodium thiocyanate (SCN^-) standard work solution with water step by step, and prepare serial standard work solution of applicable concentrations (referred linear range:

0.01 mg/L～1.0 mg/L). The standard solution is determined according to chromatography operating conditions (7.2). Based on the chromatogram, draw the standard curve with the concentration of sulfur dioxide as abscissa and the response of the peak area (or peak high) as ordinate, and calculate the linear regression equation. For chromatogram of the standard see Figure A. 1 is showed in Annex A.

7.4 Sample analysis

The sample solution is determined according to chromatography operating conditions (7.2), and the quantitative analysis is conducted on the basis of peak area (or peak high) with external standard method. The response value of the sample solution should be within the range of standard linearity.

7.5 Blank test

The operation of the blank test is the same as the described in the method of determination, but with the omission of sample addition.

8 Calculation and result presentation

The content of sodium thiocyanate (SCN^-) in the test sample is calculated by Formula (1):

$$X = \frac{(c - c_0) \times V_1 \times V_3 \times 1\,000}{m \times V_2 \times 1\,000} \quad \cdots\cdots(1)$$

Where:

X ——the content of sodium thiocyanate (SCN^-) in the test sample, mg/kg;

c ——the concentration of sodium thiocyanate (SCN^-) in sample solution, mg/L;

c_0 ——the concentration of sodium thiocyanate (SCN^-) in blank solution, mg/L;

V_1—— the volume of the sample solution with acetonitrile extration, mL;

V_3——the volume of the extration solution for diluting, mL;

m ——the mass of test sample, g;

V_2——the volume of the pipette extract solution when dillute with water, mL.

The calculation result should be remaining two significant figures.

9 Limit of detection

The method detection limit for sodium thiocyanate (SCN^-) in liquid samples is 0.25 mg/kg and 1.0 mg/kg for solid samples.

10 Recovery and precision

The recovery and precision are showed in Table B.1 of Annex B.

Gas chromatography

11 Principle

The sodium thiocyanate of sample extracted with water could become cyanogen chloride after adding Chloramine T; The determination was aceieved by headspace gas chromatography and quantified by external standard method.

12 Reagents and Materials

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

12.1 Sodium thiocyanate standard (NaSCN, CAS No.: 540-72-7): purity≥99.99%.

12.2 Zinc acetate.

12.3 Chloramine T.

12.4 Zinc acetate solution: weigh zinc acetate (12.2) 22 g, then transfer it into 100 mL volumetric flask, dillute to mark with water.

12.5 Chloramine T solution: weigh Chloramine T (12.3) 1 g, then transfer it into 100 mL volumetric flask, dillute to mark with water.

12.6 Sodium thiocyanate (SCN^-) standard storage solution (1 000 mg/L): accurately weigh sodium thiocyanate 0.136 7 g, then transfer it into 100 mL volumetric flask, dillute to mark with water. Preserve at 0 ℃ ~4 ℃ for six month.

12.7 Sodium thiocyanate (SCN^-) standard medium solution (10 mg/L): according to need, accurately pipette sodium thiocyanate standard storage solution (12.6) 1.00 mL into 100 mL volumetric flask dillute to mark with water.Preserye at 0 ℃～4 ℃ for one month.

12.8 Sodium thiocyanate(SCN^-)standard work solution:0、0.005、0.01、0.02、0.05、0.1 mg/L.

13 Apparatus and equipment

13.1 Gas chromatography:equipped with electron capture detector.

13.2 Headspace sampler.

13.3 Headspace bottle:20 mL.

13.4 Vortex mixer.

13.5 Balance:with 0.01 g and 0.000 1 g sensivity.

13.6 Centrifuge:≥4 000 r/min.

14 Sample preparation and storage

Collect a 500 g or 500 mL sample that is representative of the entire sample. The sample should be mixed directly and divided into two equal portions. Each portion is placed into a clean vessel as a test sample,which is then sealed. All the samples should be stored under 0 ℃～4℃.

15 Procedure

15.1 Sample pretreatment

Accurately weigh 1 g of the test sample (accurate to 0.01 g) into a 100 mL volumetric flask.Add 4 mL zinc acetate solution (12.4) and dillute to mark with water. Stand to 1 hour and centrifuge at 4 000 r/min for 5 min. Accurately pipette 10 mL of the supernatant into headspace bottle,add 0.1 mL Chloramine T solution (12.5) and mix for test.

15.2 Chromatography operating conditions

15.2.1 The condition of headspace gas chromatography was showed in Annex C.

15.2.2 GC operating conditions:

a) Chromatographic column: capillary column, BP10 25 m × 0.32 mm (id) × 0.50 μm(film thickness);

b) Temperature programme: 40 ℃ (keep 5 min), 50 ℃/min to 200 ℃ (keep 2 min);

c) Carrier gas: Nitrogen (purity≥99.999%);

d) Injection port temperature: 150 ℃;

e) Detector temperature: 260 ℃;

f) Split ratio: 100 : 1;

g) Flow rate: 1.0 mL/min.

15.3 Standard Curve

Accurately pipette 10 mL of the sodium thiocyanate standard work solution (12.8) into headspace bottle, add 0.1 mL Chloramine T solution and mix for test. The standard solution are determined according to chromatography operating conditions (15.2). Based on the chromatogram, draw the standard curve with the concentration of sulfur dioxide as abscissa and the response of the peak area (or peak high) as ordinate, and calculate the linear regression equation condition, the retention time of sodium thiocyanate ion derivative is about 2.50 min, For chromatogram of the standard see Figure A.2 in Annex A.

15.4 Sample analysis

The standard solution and the sample are determined according to chromatography operating conditions (15.2), and the quantitative analysis is conducted on the basis of peak area of sodium thiocyanate ion derivative with external standard method. The responses of the standard solution and the sample should be in the linearity of the instrument.

15.5 Blank test

The operation of the blank test is the same as the described in the method of determination, but with the omission of sample addition.

15.6 Calculation and result presentation

The content of sodium thiocyanate in the test sample is calculated by Formula (2):

$$X = \frac{(c - c_0) \times V \times 1\,000}{m \times 1\,000} \qquad \cdots\cdots(2)$$

Where:

X ——the content of sodium thiocyanate (SCN^-) in the test sample, mg/kg;

c ——the concentration of sodium thiocyanate (SCN^-) in the sample solution, mg/L;

c_0 ——the concentration of sodium thiocyanate (SCN^-) in the blank solution, mg/L;

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

m ——mass of test sample, g.

The calculation result should be remaining one significant figures.

16 Limit of detection

The method detection limit for sodium thiocyanate (SCN^-) in dairy products is 1.0 mg/kg.

17 Recovery and precision

The recovery and precision are showed in Table B.2 of Annex B.

Annex A
(Informative)
Chromatogram of the standard

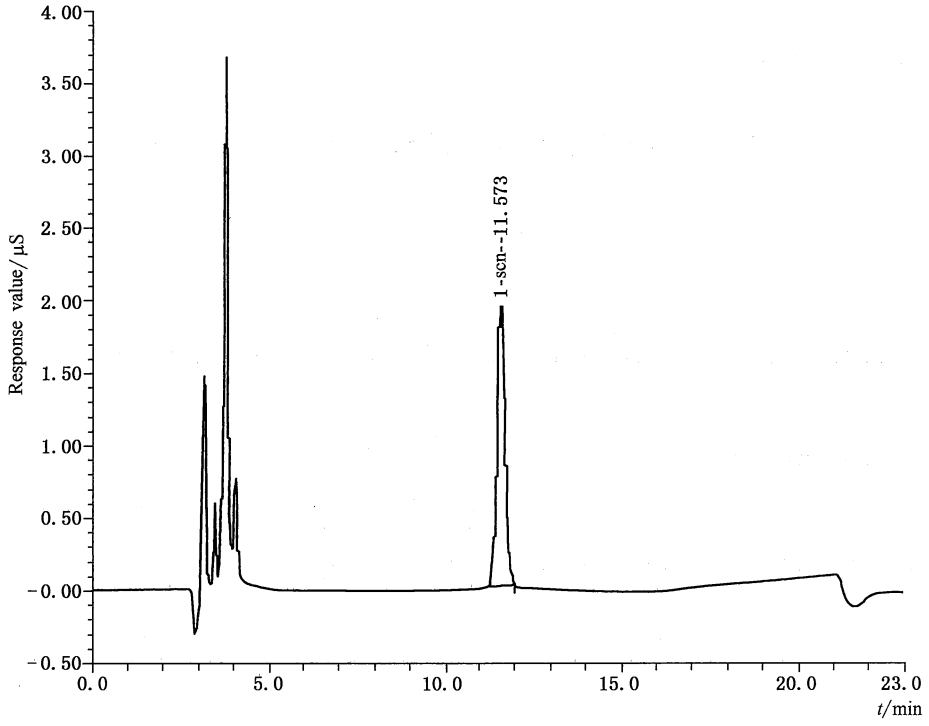

Figure A.1 Ion chromatogram of sodium thiocyanate (1 mg/L)

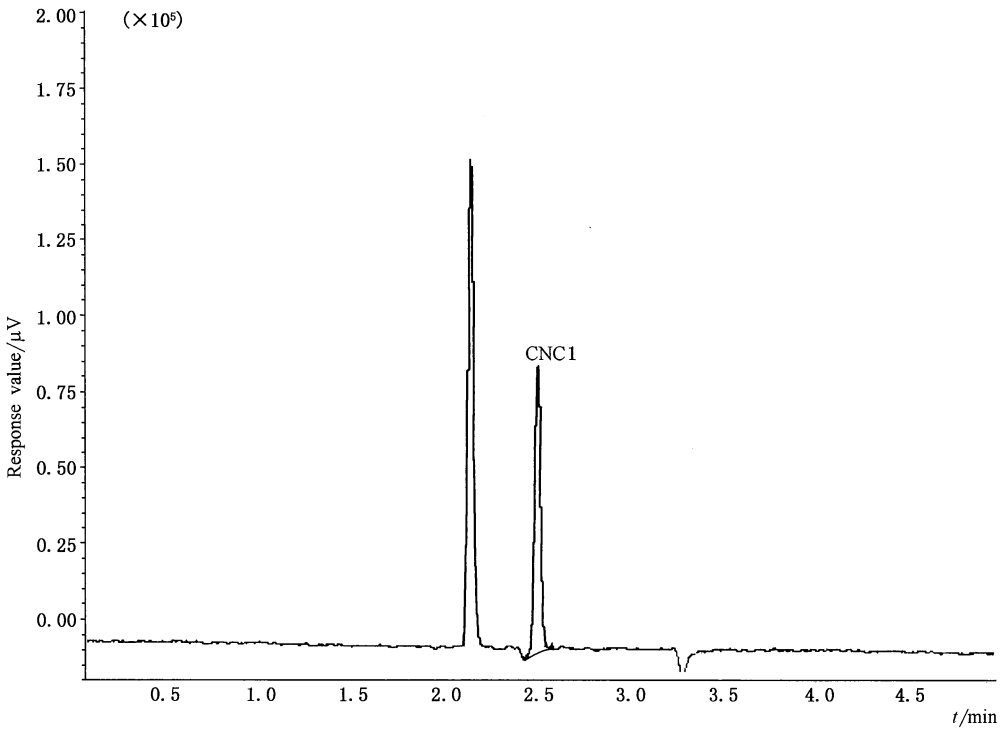

Figure A.2 Gas chromatogram of sodium thiocyanate ion derivative (0.01 mg/L)

Annex B
(Informative)
Data of recovery and precision

Table B.1 Recovery and Precision (Ion Chromatogram)

Sample	Fortified concentration (mg/kg)	Recovery %	RSD %
Sterilized milk	0.25	80.4～100.2	6.45
	0.50	92.3～104.1	4.89
	2.50	93.2～101.2	2.99
Pasteurized milk	0.25	88.6～105.5	6.31
	0.50	88.9～105.8	5.43
	2.50	90.6～103.8	4.61
Yoghurt	0.25	88.3～104.4	5.35
	0.50	92.8～106.0	4.83
	2.50	90.4～101.2	4.15
Formula milk	0.25	87.5～105.1	7.78
	0.50	88.2～104.1	7.74
	2.50	90.8～104.4	4.74
Milk beverage	0.25	86.1～108.7	8.36
	0.50	86.6～104.2	6.94
	2.50	91.6～102.8	3.70
Milk powder	1.00	90.4～105.6	5.59
	2.00	91.3～103.3	4.84
	10.00	91.8～102.7	3.90
Formula milk powder	1.00	91.7～104.3	4.73
	2.00	92.1 ～98.5	2.57
	10.00	92.1～103.7	3.95
Cheese	1.00	90.9～102.6	4.31
	2.00	91.5～105.7	5.08
	10.00	95.2～104.5	3.31
Condensed milk	1.00	91.1～104.7	4.58
	2.00	93.1～105.5	4.24
	10.00	92.2～103.9	4.72

Table B.2 Recovery and Precision (Gas Chromatogram)

Sample	Fortified concentration (mg/kg)	Recovery %	RSD %
Pasteurized milk	1.0	94.0～110.0	5.36
	2.0	90.5～108.5	5.60
	10.0	90.2～107.3	7.49
Yoghurt	1.0	90.0～110.0	6.86
	2.0	90.5～108.5	6.78
	10.0	90.1～107.2	6.22
Milk powder	1.0	91.0～109.0	6.86
	2.0	91.5～106.5	5.07
	10.0	90.4～109.1	7.39
Milk beverage	1.0	91.0～110.0	7.53
	2.0	90.5～108.5	7.37
	10.0	93.1～109.3	4.98
Cheese	1.0	93.0～110.0	5.47
	2.0	94.5～108.5	3.91
	10.0	90.2～109.3	7.89
Formula milk	1.0	92.0～109.0	5.92
	2.0	93.5～110.0	6.30
	10.0	92.1～108.4	5.42

Annex C
(Informative)
Headspace sampler operating condition[1)]

Headspace sampler operating conditions are as follows:

a) Temperature of headspace balance:35 ℃;

b) Temperature of sample needle:110 ℃;

c) Temperature of transmission line:120 ℃;

d) Time of headspace heating:20 min;

e) Time of sampling:0.03 min;

f) Time of pressurize:2.5 min;

g) Carrier gas:12.5 psi (1 psi=6.895 kPa).

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1) Non-commercial statement:The parameters of Annex C are acquired from PE Turbo Matrix 16 and only are used for reference. The equipments and their types involved in the standard method are not related to commercial aims,and it is encouraged to use equipments of different corporation or different type.

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