

# 乳制品中三聚氰胺检测方法的现状及研究进展

祝海珍\*

(南京旅游职业学院 烹饪与营养学院, 南京 211100)

**摘 要:** 三聚氰胺是一种三嗪类含氮杂环有机化合物, 三聚氰胺分子中含氮量达 66.7%, 一些不法企业将其添加到牛奶、乳制品中, 造成粗蛋白质虚高的假相, 不仅对乳制品、养殖业等产业产生不利影响, 对人类健康也构成严重威胁。因此, 对乳制品中三聚氰胺的检测方法的研究, 在食品安全检测方面早已成为了社会的热点。本文着重论述了近年来乳制品中三聚氰胺检测方法的研究现状, 检测方法主要包括液相色谱-质谱联用法、气相色谱-质谱法、表面增强拉曼光谱、电化学分析方法、红外光谱法和荧光光度法等。随着仪器和科学技术的发展, 开发操作简单、成本低廉、方便携带、准确快速、灵敏高效的乳制品中三聚氰胺的检测技术, 是今后三聚氰胺技术研究的重要方向。

**关键词:** 乳制品; 三聚氰胺; 液相色谱-质谱法; 气相色谱-质谱法

## Current situation and research progress of detection methods of melamine in dairy products

ZHU Hai-Zhen\*

(Cooking and Nutrition School, Nanjing Institute of Tourism and Hospitality, Nanjing 211100, China)

**ABSTRACT:** Melamine is a triazine-type nitrogen-containing heterocyclic organic compound. The nitrogen content in the melamine molecule reaches 66.7%. Some illegal companies add it to milk and dairy products, causing the false appearance of high crude protein. The aquaculture and other industries have adverse effects and pose a serious threat to human health. Therefore, the research on the detection method of melamine in dairy products has become a hot spot in the society in terms of food safety detection. This article focused on the research status of detection methods of melamine in dairy products in recent years. The detection methods mainly included liquid chromatography-mass spectrometry, gas chromatography-mass spectrometry, surface enhanced Raman spectroscopy, electrochemical analysis methods, infrared spectroscopy and fluorescence photometry, *etc.* With the development of instruments and science and technology, the development of simple, low-cost, portable, accurate, fast, sensitive and efficient detection technology for melamine in dairy products is an important direction for future melamine technology research.

**KEY WORDS:** dairy products; melamine; liquid chromatography-mass spectrometry; gas chromatography-mass spectrometry

## 0 引 言

俗话说“民以食为天, 食以安为先”。但是近年来, 食

品安全事件频频曝光, 消费者的身体健康屡遭食品安全的考验, 其中 2008 年的“三聚氰胺事件”最为轰动, 引发我国食品安全法变革。

\*通信作者: 祝海珍, 博士, 副教授, 主要研究方向为食品营养与卫生安全。E-mail: zhuhai zhen1979@sina.com

\*Corresponding author: ZHU Hai-Zhen, Ph.D, Associate Professor, Cooking and Nutrition School, Nanjing Institute of Tourism and Hospitality, Nanjing 211100, China. E-mail: zhuhai zhen1979@sina.com

三聚氰胺(melamine), 化学式为  $C_3N_3(NH_2)_3$ , 结构式见图 1, 被命名为 1,3,5-三嗪-2,4,6-三胺, 是一种三嗪类含氮杂环有机化合物。长期或反复大量摄入三聚氰胺可能对肾与膀胱产生影响, 导致产生结石。三聚氰胺结石微溶于水, 成年人由于经常喝水使得结石不容易形成, 而哺乳期婴儿由于喝水很少, 并且其肾脏比成年人肾脏狭小, 故更容易形成结石。

GB 5009.5—2016《食品安全国家标准 食品中蛋白质的测定》<sup>[1]</sup>中第一法“凯氏定氮法”测定食品中粗蛋白质的含量, 即以含氮量的多少乘以 6.25 得出蛋白质含量。然而应用凯氏定氮法只能用来检测食品中的氮含量, 并不能区分蛋白氮和三聚氰胺的氮含量。一些无良商人为地在食品中添加三聚氰胺以提高其含氮量, 从而达到降低生产成本以牟取暴利为目的。最为典型的事例即为 2007 年“美国宠物毒粮事件”和 2008 年“中国毒奶粉事件”。

因此本文主要对乳制品中的三聚氰胺检测技术的研究现状进行详细阐述, 并对其发展方向进行展望, 以期为消费者更为深入地了解三聚氰胺及三聚氰胺检测方法的推广和开发奠定基础。

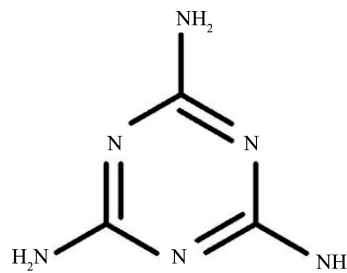


图 1 三聚氰胺的结构式

Fig.1 Structural formula of melamine

## 1 三聚氰胺的检测技术

### 1.1 液相色谱-质谱联用法

液相色谱-质谱联用法(liquid chromatograph-mass spectrometer, LC-MS)是用液相色谱法分离与用质谱法定性相联用的分析方法, 结合了液相色谱仪有效分离热不稳定性及高沸点化合物的分离能力与质谱仪很强的组分鉴定能力, 此法分析时间短、效率高、自动化程度高、不仅可以排除基质干扰, 而且还能提供待测物的结构信息, 是目前国内外应用最多的检测手段, 本文综述了近年来部分液相色谱-质谱联用法检测奶制品中三聚氰胺的研究文献, 详见表 1。

表 1 液相色谱-质谱法检测奶制品中三聚氰胺的实验参数  
Table 1 Experimental parameters of the LC-MS method for detecting melamine in dairy products

仪器型号	色谱柱	流动相条件	检出限/定量限 ( $\mu\text{g}/\text{kg}$ )	回收率 /%	精密度 /%	参考文献
美国 Waters 液相色谱-质谱联用仪	Waters Atlantis HILIC Silica 色谱柱	10 mmol/L 乙酸铵+乙腈	0.2	92.5~97.2	0.4~5.1	[2]
Ultimate 3000 system 超高效液相色谱质谱联用仪	Waters BEH HILIC analytical 色谱柱	0.1% 甲酸和 4 mmol/L 甲酸铵的水/乙腈溶液	2.0	78.1~107.1	1.4~7.9	[3]
Agilent 6410 Triple Quad 液相色谱-质谱联用仪	Zorbax RX-SIL 色谱柱	乙腈+5 mmol/L 甲酸铵水溶液(90:10, V:V)	10	90~110	4.32	[4]
Agilent 6410 串联三级四极杆质谱仪	$C_{18}$ 色谱柱	0.1% 七氟丁酸(HFBA)水溶液(体积分数)-甲醇(70:30, V:V)	0.1	96.94~101.67	<1.87	[5]
美国 Agilent 6310 Ion Trap 液相色谱-质谱联用仪	亲水性反相 $C_8$ 柱	离子对试剂缓冲液:乙腈(85:15, V:V)	200	91.6~104.2	1.2~2.6	[6]
Agilent 1200SL 快速液相色谱-6410 三重四极杆质谱仪	强阳离子交换与反相 $C_{18}$ 混合填料	等体积比的 10 mmol/L 乙酸铵水溶液和乙腈(用甲酸调节至 pH=3.0)	10	80.4~107.4	$\leq 9.4$	[7]
SCIEX Triple Quad 4500 液相色谱-质谱联用仪	MN Nu cleoshell Hilic 色谱柱	流动相 A:0.005 mol/L 乙酸铵溶液-乙腈(50:50, V:V)流动相 B:0.1% 甲酸水溶液-乙腈(5:95, V:V)	2.0	82.37~103.15	<6	[8]
Agilent 1200 快速液相色谱-G6410B 质谱仪	Waters Hilic 色谱柱	含 5 mmol/L 乙酸铵的乙腈(95:5, V:V)溶液	1.7	99.8~102	1.9~3.2	[9]
Agilent 6410 串联三级四极杆质谱仪	Agilent Eclipse XDB- $C_8$ 柱	0.05% 氨水的流动相	1.0	83.0~102.5		[10]

## 1.2 气相色谱-质谱法

气相色谱-质谱法(gas chromatography-mass spectrometry, GC-MS)是将气相色谱和质谱结合构成的一种仪器联用分析技术,是用气相色谱分离复杂的混合物样品,使其中的化合物逐个地进入质谱仪的离子源,可用电子轰击,或化学离子化等方法,使每个样品中所有的化合物都离子化,结合标样或标准谱图,具有分析高效快速,定量定性准确等特点。

PAN 等<sup>[11]</sup>将牛奶用乙腈/水的混合物萃取,通过 GC-MS 用三聚氰胺-<sup>13</sup>C<sub>3</sub> 做内标进行定量,检出限为 0.25 mg/kg,回收率为 80.8%~101.5%,相对标准偏差(relative standard deviation, RSD)为 3.6%~7.9%。金春爱等<sup>[12]</sup>采用三氯乙酸溶液提取牛奶中的三聚氰胺,选择离子监测模式,外标法定量,建立气相色谱-质谱联用法测定牛奶中三聚氰胺的含量,检测限达 1 μg/kg,回收率达 90%~110%,RSD 达 0.3%~6%。曹艳平等<sup>[13]</sup>采用反吹技术和三重串联四极杆气相色谱质谱法测定婴幼儿奶粉及乳制品中三聚氰胺的含量,线性范围为 1~50 ng,样品添加回收率为 89.2%~103%,RSD 为 5.07%和 2.90%,样品最终检出限为 12 μg/kg。

## 1.3 表面增强拉曼光谱

拉曼光谱,又称拉曼散射(Raman scattering, RS),是一种分子受光子激发的非弹性散射现象,最早是由印度物理学家拉曼(Chandrasekhara Venkata Raman)在 1928 年用单色光照射 CCl<sub>4</sub> 液体时发现<sup>[14]</sup>。

1974 年, FLEISHMANN 等<sup>[15]</sup>首次报道了吸附在用电化学方法粗糙化的银电极表面的吡啶分子在不同电位下的拉曼光谱,表明了拉曼光谱能与电化学方法联用而测得吸附在电极表面的分子的信息。将与银、金、铜等粗糙金属相互作用后使拉曼光谱增强效应称为表面增强(surface enhanced Raman scattering, SERS)效应,对应的光谱称为表面增强拉曼光谱。表面增强拉曼光谱技术使其检测限提高了 4 至 10 个数量级,甚至可达十亿分之一(10<sup>-12</sup> g/g)<sup>[16]</sup>。

近年来,很多学者<sup>[17-24]</sup>研究了表面增强拉曼光谱法测定乳制品中三聚氰胺含量的方法。冯彦婷等<sup>[21]</sup>以金属钛板作为 SERS 衬底材料,在质量浓度 0.2~10 mg/L 的范围内,SERS 强度随着牛奶中三聚氰胺浓度的增大而增强,线性相关系数  $r^2=0.998$ ,检测限为 0.08 mg/L, RSD 为 4.34%。PINYI 等<sup>[24]</sup>将 CD-AgNP 用作表面增强拉曼光谱中的底物,校正图的相关系数为 0.9995,检出限为 3.0 μg/L,相对标准偏差<10%,回收率在 89%~104%。RAJAPANDIYAN 等<sup>[22]</sup>利用装饰在圆柱形支撑物上的银纳米颗粒(AgNP),分析乳汁和奶粉中的三聚氰胺,成功地采用了稀释方法以抑制真实样品中的基质效应,使检测限提高。NIE 等<sup>[23]</sup>研究发现 Au/Ag BPHAN 阵列在三聚氰胺分子的检测中显示出很大

的 SERS 活性,当 Au 与 Ag 的比例接近 1:1 时,SERS 强度约为 Ag 或 Au 样品的 5 倍,比美国 FDA 规定的婴儿乳制品的耐受水平低 10 倍,比最严格的标准低 1.5 倍。

## 1.4 电化学分析方法

电化学分析法是将试液作为化学电池的一个组成部分,根据该电池的某种电参数(如电阻、电导、电位、电流、电量或电流-电压曲线等)与被测物质的浓度之间存在一定的关系而进行测定的方法。电化学分析法包括极谱法、电极法和毛细管电泳法等,具有灵敏度高,准确度高,仪器设备较简单,价格低廉,容易实现自动化等特点。

李萌萌等<sup>[25]</sup>利用氧化石墨烯修饰电极与三聚氰胺之间有氢键作用,使响应电信号增强,峰电流值变大,该方法检测范围在  $1.0 \times 10^{-7} \sim 1.0 \times 10^{-3}$  mol/L,最低检测限是为  $1.0 \times 10^{-8}$  mol/L,回收率为 98.3%~99.95%。马妍等<sup>[26]</sup>用线性循环伏安法测定了牛奶粉中三聚氰胺的含量,线性相关系数( $r^2$ )大于 0.99,相对标准偏差为 0.65%,样品加标回收率为 98.0%~107.3%。ZHAO 等<sup>[27]</sup>研究基于壳聚糖与聚乙烯吡咯烷酮分散的还原氧化石墨烯(CTS-PVP-rGO)、金纳米颗粒(AuNPs)和金属有机骨架 MIL-101 的复合物,通过自组装成功构建了高灵敏度的三聚氰胺电化学传感器,在 pH 7.0,扫描速率为 100 mV/s 和频率为 50 Hz 的情况下,三聚氰胺的测定极限低至  $5.00 \times 10^{-11}$  mol/L,线性范围为  $5.00 \times 10^{-11} \sim 1.00 \times 10^{-8}$  mol/L,相关系数( $r$ )为 0.996。

## 1.5 红外光谱法

红外光谱法,又称“红外分光光度分析法”,是分析利用红外光谱对物质分子进行的分析和鉴定。红外光谱在固、液、气态样均可用,且用量少,不破坏样品,分析速度快,可以实现在线分析,分析灵敏度较高,但分析误差较大。

CHEN 等<sup>[28]</sup>研究了近红外光谱(near infrared spectrum, NIR)和一类偏最小二乘法(one-class partial least squares, OCPLS)检测三聚氰胺掺假的可行性,实验结果总准确率为 89%,灵敏度为 90%,特异性为 88%,均能达到满意的效果。张青青等<sup>[29]</sup>在 1400~1600 nm 和 1900~2400 nm 波段内,利用二阶导数+Savitzky-Golay 9 点平滑的预处理方法下,当主成分数为 5 时,交叉验证相关系数为 0.9652,交叉验证均方差为 8.22,外部验证结果预测偏差均小于 5%,模型预测性能良好。白静等<sup>[30]</sup>先经过图谱分析确定特征吸收峰,结合二阶最小二乘法建立红外光谱法快速检测奶粉中三聚氰胺的线性模型,相关系数为 0.999,最低检出限为 0.7442 g/100 g。

## 1.6 荧光光度法

荧光光度法就是一种利用物质散发出来的荧光而对其实施检测的方法,其光谱范围一般处于 X 光谱区和红外光谱区。荧光光度法具有灵敏度高、选择性强、重现性好

等优点,但是利用荧光光度法对食品进行检测时,被检测物质可散发出荧光或加入试剂后能够发出荧光方能检测。

近年来,很多学者<sup>[31-33]</sup>开始研究荧光法检测乳制品中三聚氰胺含量。LI等<sup>[34]</sup>以CsPbBr<sub>3</sub> NCs @ BaSO<sub>4</sub>作为信号读数,开发了一种超灵敏的荧光纳米传感器,通过操纵柠檬酸盐保护的纳米颗粒(AuNPs)的内部过滤作用来开启三聚氰胺的测定。三聚氰胺的检测范围5.0~500.0 nmol/L,重复测定500.0 nmol/L三聚氰胺溶液( $n=11$ )的检出限为0.42 nmol/L,相对标准偏差为4.0%。WANG等<sup>[35]</sup>研究发现基于N-甲基间卟啉IX(NMM)/G-四链体结构可以用作检测牛奶样品中三聚氰胺的信号报告基因,该方法的线性范围为0.05~1 μmol/L( $r^2=0.98$ ),检出限为12.5 nmol/L,远低于婴儿配方食品允许的最大水平。张沛等<sup>[36]</sup>利用天然食品分析物鸡蛋膜作为生物膜基质,建立一种固定荧光素到鸡蛋膜上的生物传感器并用于三聚氰胺检测的方法,优化传感器体系中的荧光素浓度及戊二醛质量分数,鸡蛋膜传感器的线性工作范围为1~500 μg/L,检出限为0.47 μg/L,并将鸡蛋膜荧光传感器成功应用于市售奶制品中三聚氰胺的检测。

## 2 其他方法

乳制品中三聚氰胺的检测方法还有高效液相色谱法<sup>[37-42]</sup>,分光光度法<sup>[43-45]</sup>,酶联免疫法<sup>[46-48]</sup>,传感器法<sup>[49-51]</sup>等,本文不做详细论述。

## 3 结论与展望

三聚氰胺,作为有机化工的中间产品,由于其含氮高,时有被非法用作食品添加剂,以提高奶制品的含氮量。三聚氰胺虽然毒性低,但在婴幼儿体内易形成结石。乳制品中三聚氰胺的检测方法有液相色谱-质谱法、气相色谱-质谱法、表面增强拉曼光谱法、电化学分析法、红外光谱法和荧光光度法等,这些方法的仪器和实验室要求较高,对检测人员能力的要求也较高,不易成为人们日常检测技术。因此,乳制品中三聚氰胺的检测技术需要进一步深入研究,随着仪器和科学技术的发展,开发操作简单、成本低廉、方便携带、准确快速、灵敏高效的乳制品中三聚氰胺的检测技术,以便满足日常生活的需要和应用,是今后三聚氰胺技术研究的重要方向。

## 参考文献

- [1] GB 5009.5—2016 食品安全国家标准 食品中蛋白质的测定[S]. GB 5009.5—2016 National food safety standard-Determination of protein in food [S].
- [2] WANG Y, GAO L, QIN DL, *et al.* Analysis of melamine in milk powder by CNT-MIP with matrix solid phase dispersion and LC-MS/MS [J]. Food Anal Method, 2017, 10(5): 1386-1396.
- [3] CHEN DW, ZHAO YF, MIAO H, *et al.* A novel dispersive micro solid phase extraction using PCX as the sorbent for the determination of melamine and cyromazine in milk and milk powder by UHPLC-HRMS/MS [J]. Talanta, 2015, (134): 144-152.
- [4] 赵慧芬, 水明, 张雪林, 等. 液相色谱-质谱/质谱法测定乳品中三聚氰胺含量的简便方法[J]. 中国奶牛, 2009, (1): 43-46. ZHAO HF, SHUI M, ZHANG XL, *et al.* A simple method for the determination of melamine in dairy products by liquid chromatography-mass spectrometry/mass spectrometry [J]. Chin Dairy Cattle, 2009, (1): 43-46.
- [5] 吴庆庆, 范可心, 沙伟, 等. 基于反相液相色谱-质谱联用的高灵敏度三聚氰胺检测新方法[J]. 科学通报, 2009, (2): 171-176. WU QQ, FAN KX, SHA W, *et al.* A new high-sensitivity detection method for melamine based on reversed-phase liquid chromatography-mass spectrometry [J]. Chin Sci Bull, 2009, (2): 171-176.
- [6] 蒋伯成, 张剑平, 于秋影. 液相色谱质谱联用法快速测定配方奶粉中的三聚氰胺[J]. 高师理科学刊, 2009, 29(3): 51-53. JIANG BC, ZHANG JP, YU QY. Rapid determination of melamine in formula milk powder by liquid chromatography-mass spectrometry [J]. J Sci Norm Univ, 2009, 29(3): 51-53.
- [7] 陈冬东, 彭涛, 李晓娟, 等. 液相色谱-质谱/质谱法测定乳与乳制品中的三聚氰胺[J]. 中国食品卫生杂志, 2009, 21(3): 253-255. CHEN DD, PENG T, LI XJ, *et al.* Determination of melamine in milk and dairy products by liquid chromatography-mass spectrometry/mass spectrometry [J]. Chin J Food Hyg, 2009, 21(3): 253-255.
- [8] 黄坤, 陈冉, 范小龙, 等. 同位素内标-超高效液相色谱串联质谱法快速测定含乳饮料中三聚氰胺残留[J]. 中国乳品工业, 2019, 47(8): 50-53. HUANG K, CHEN R, FAN XL, *et al.* Rapid determination of melamine residues in dairy beverages by isotope internal standard-ultra performance liquid chromatography tandem mass spectrometry [J]. Chin Dairy Ind, 2019, 47(8): 50-53.
- [9] 初晓娜, 矫秀燕, 穆阿丽, 等. 高效液相色谱-串联质谱法测定生鲜乳中三聚氰胺的含量[J]. 理化检验, 2015, 51(3): 394-397. CHU XN, JIAO XY, MU AL, *et al.* Determination of melamine in fresh milk by high performance liquid chromatography-tandem mass spectrometry [J]. Phys Test Chem Anal, 2015, 51(3): 394-397.
- [10] ALAA K. Optimized extraction method for LC-MS determination of bisphenol A, melamine and di(2-ethylhexyl) phthalate in selected soft drinks, syringes, and milk powder [J]. J Chromatogr B, 2013, 930: 98-103.
- [11] PAN XD, WU PG, YANG DJ, *et al.* Simultaneous determination of melamine and cyanuric acid in dairy products by mixed-mode solid phase extraction and GC-MS [J]. Food Control, 2013, 30(2): 545-548.
- [12] 金春爱, 王玉方, 罗婧, 等. 牛奶中三聚氰胺的气相色谱-质谱联用快速测定[J]. 中兽医学杂志, 2014, (7): 49-50. JIN CA, WANG YF, LUO J, *et al.* Rapid determination of melamine in milk by gas chromatography-mass spectrometry [J]. Chin J Vet Med, 2014, (7): 49-50.
- [13] 曹艳平, 吴王思森, 李蔚. 采用反吹技术和 GC-MS/MS 测定婴幼儿奶粉及乳制品中三聚氰胺[J]. 中国卫生检验杂志, 2015, 25(4): 480-482. CAO YP, WU WWSM, LI W. Determination of melamine in infant milk powder and dairy products by backflushing technology and GC-MS/MS

- [J]. *Chin J Health Lab Technol*, 2015, 25(4): 480–482.
- [14] RAMAN CV, KRISHNAN KS. A new type of secondary radiation [J]. *Nature*, 1928, (121): 501–502.
- [15] FLEISCHMANN M, HENDRA PJ, MCQUILLAN AJ. Raman spectra of pyridine adsorbed at a silver electrode [J]. *Chem Phys Lett*, 1974, 26(2): 163–166.
- [16] WANG HH, LIU CY, WU SB, *et al.* Highly Raman-enhancing substrates based on silver nanoparticle arrays with tunable sub-10 nm gaps [J]. *Adv Mater*, 2010, 18(4): 491–495.
- [17] AKASHA, KALEEM, MEHMOONA, *et al.* GMA-EDMA monolith gold nanoparticles melamine SERS [J]. *Food Chem*, 2018, 277: 624–631.
- [18] KALEEM A, AZMAT M, SHARMA A, *et al.* Melamine detection in liquid milk based on selective porous polymer monolith mediated with gold nanospheres by using surface enhanced Raman scattering [J]. *Food Chem*, 2019, 277: 624–631.
- [19] XIAO G, LI L, YAN A, *et al.* Direct detection of melamine in infant formula milk powder solution based on SERS effect of silver film over nanospheres [J]. *Spectrochim Acta A*, 2019, 223. DOI: 10.1016/j.saa.2019.117269
- [20] XU DP, KANG WQ, ZHANG S, *et al.* Quantitative determination of melamine in milk by surface-enhanced Raman scattering technique based on high surface roughness silver nanosheets assembled by nanowires [J]. *Microchem J*, 2019, 148: 190–196.
- [21] 冯彦婷, 林沛纯, 谢慧凤, 等. 基于纳米银颗粒团聚反应的表面增强拉曼光谱法测定牛奶中三聚氰胺的含量[J]. *食品与发酵工业*, 2019, 45(15): 256–261.
- FENG YT, LIN PC, XIE HF, *et al.* Surface-enhanced Raman spectroscopy based on the agglomeration of silver nanoparticles to determine the content of melamine in milk [J]. *Food Ferment Ind*, 2019, 45(15): 256–261.
- [22] RAJAPANDIYAN P, TANG WL, YANG J. Rapid detection of melamine in milk liquid and powder by surface-enhanced Raman scattering substrate array [J]. *Food Control*, 2015, 56: 155–160.
- [23] NIE B, LUO Y, SHI J, *et al.* Bowl-like pore array made of hollow Au/Ag Alloy nanoparticles for SERS detection of melamine in solid milk powder [J]. *Sens Actuat B Chem*, 2019, 301. DOI: 10.1016/j.snb.2019.127087
- [24] PINYI M, LIANG FH, SUN Y, *et al.* Rapid determination of melamine in milk and milk powder by surface-enhanced Raman spectroscopy and using cyclodextrin-decorated silver nanoparticles [J]. *Microchim Acta*, 2013, (180): 1173–1180.
- [25] 李萌萌, 李冬迪, 罗仙科, 等. 层层自组装复合电极用于检测牛奶中三聚氰胺[J]. *沈阳化工大学学报*, 2018, 32(3): 242–249.
- LI MM, LI DD, LUO XK, *et al.* Layer-by-layer self-assembled composite electrode for the detection of melamine in milk [J]. *J Shenyang Univ Chem Technol*, 2018, 32(3): 242–249.
- [26] 马妍, 申远, 王川, 等. 基于银纳米粒子-多壁碳纳米管/玻碳电极的电化学法测定奶粉中三聚氰胺[J]. *分析科学学报*, 2019, 35(4): 455–460.
- MA Y, SHEN Y, WANG C, *et al.* Determination of melamine in milk powder by electrochemical method based on silver nanoparticles-multi-wall carbon nanotubes/glassy carbon electrode [J]. *J Anal Sci*, 2019, 35(4): 455–460.
- [27] ZHAO RC, SUN S, HAO W, *et al.* A highly sensitive determination for the melamine in milk on MIL-101/AuNPs/CTS-PVP-rGO/GCE electrochemical sensor [J]. *Russ J Electrochem*, 2019, 55(7): 651–662.
- [28] CHEN H, TAN C, LIN Z, *et al.* Detection of melamine adulteration in milk by near-infrared spectroscopy and one-class partial least squares [J]. *Spectrochim Acta A*, 2017, (173): 832–836.
- [29] 张青青, 沈晓芳, 柴俊宇, 等. 基于 MEMS 微镜技术的近红外光谱检测奶粉中的三聚氰胺[J]. *食品工业*, 2018, 39(12): 135–138.
- ZHANG QQ, SHEN XF, CHAI JY, *et al.* Detection of melamine in milk powder by near infrared spectroscopy based on MEMS micromirror technology [J]. *Food Ind*, 2018, 39(12): 135–138.
- [30] 白静, 王会. 红外光谱法测定奶粉中三聚氰胺和尿素[J]. *食品与发酵工业*, 2020, 46(8): 267–272.
- BAI J, WANG H. Determination of Melamine and Urea in Milk Powder by Infrared Spectroscopy [J]. *Food Ferment Ind*, 2020, 46(8): 267–272.
- [31] XU L, LI DX, JIANG BY, *et al.* Melamine-mediated base mismatch for label-free and amplified sensitive fluorescent detection of melamine in milk [J]. *Food Anal Method*, 2019, 12(5): 1255–1261.
- [32] HU XT, SHI JY, SHI YQ, *et al.* Use of a smart phone for visual detection of melamine in milk based on Au@Carbon quantum dots nanocomposites [J]. *Food Chem*, 2019, 272: 58–65.
- [33] 常晨阳, 常凯, 刘丽蓉, 等. 氧化石墨烯-DNA 纳米荧光探针用于检测牛奶中的三聚氰胺[J]. *中国动物检疫*, 2018, 35(12): 101–104.
- CHANG CY, CHANG K, LIU LR, *et al.* Graphene oxide-DNA nano-fluorescence probe for the detection of melamine in milk [J]. *Chin Anim Quarant*, 2018, 35(12): 101–104.
- [34] LI Q, WANG H, YUE X, *et al.* Perovskite nanocrystals fluorescence nanosensor for ultrasensitive detection of trace melamine in dairy products by the manipulation of inner filter effect of gold nanoparticles [J]. *Talanta*, 2020, 211. DOI:10.1016/j.talanta.2019.120705
- [35] WANG JJ, WU Y, WU Q, *et al.* Highly sensitive detection of melamine in milk samples based on N-methylmesoporphyrin IX/G-quadruplex structure [J]. *Microchem J*, 2020, 155. DOI: 10.1016/j.microc.2020.104751
- [36] 张沛, 李莹, 王增利, 等. 鸡蛋膜荧光传感器光谱信息表征及三聚氰胺检测方法的构建[J]. *食品科学*, 2018, 39(22): 328–333.
- ZHANG P, LI Y, WANG ZL, *et al.* Spectral information characterization of egg film fluorescence sensor and construction of melamine detection method [J]. *Food Sci*, 2018, 39(22): 328–333.
- [37] MALEKIA J, NAZARIB F, YOUSEFIA J, *et al.* Determinations of melamine residue in infant formula brands available in iran market using by HPLC method [J]. *Iran J Pharm Res* 2018, 17(2): 563–570.
- [38] FASHI A, YAFTIAN MR, ZAMANI A. Determination of melamine in dairy products using electromembrane-LPME followed by HPLC [J]. *Food Chem*, 2015, 188(1): 92–98.
- [39] 李英杰, 郑玉山, 周晋尧, 等. 高效液相色谱法测定奶粉质控样品中三聚氰胺的含量及其不确定度分析[J]. *食品安全质量检测学报*, 2020, 11(3): 950–954.
- LI YJ, ZHENG YS, ZHOU JY, *et al.* Determination of melamine in milk powder quality control samples by high performance liquid chromatography and uncertainty analysis [J]. *J Food Saf Qual*, 2020, 11(3): 950–954.
- [40] RAMEZANI AM, AHMADI R, ABSALAN G. Designing a sustainable mobile phase composition for melamine monitoring in milk samples based

- on micellar liquid chromatography and natural deep eutectic solvent [J]. *J Chromatogr A*, 2020, 1610. DOI: 10.1016/j.chroma.2019.460563
- [41] 王新喜. 乳与乳制品中三聚氰胺的快速检测-高效液相色谱法[J]. *食品安全导刊*, 2017, (21): 125-126.  
WANG XX. Rapid detection of melamine in milk and dairy products-high performance liquid chromatography [J]. *Chin Food Saf Magaz*, 2017, (21): 125-126.
- [42] SRIMATHI R, PRIYA D, KUMAR BS. Determination of melamine in Indian milk and dairy products by reverse phase liquid chromatography [J]. *R J Phar Techno*, 2017, 10(12): 4269-4272.
- [43] CHEN XY, HA W, SHI YP. Sensitive colorimetric detection of melamine in processed raw milk using asymmetrically PEGylated gold nanoparticles [J]. *Talanta*, 2019, 194: 475-484.
- [44] 孔英戈, 张少云, 潘萍, 等. 基于纳米金颗粒团聚反应的分光光度法测定牛奶中三聚氰胺的含量[J]. *理化检验*, 2018, 54(11): 1303-1307.  
KONG YG, ZHANG SY, PAN P, *et al.* Spectrophotometric determination of melamine in milk based on the agglomeration reaction of gold nanoparticles [J]. *Phys Test Chem Anal*, 2018, 54(11): 1303-1307.
- [45] 赵静, 李永生, 高秀峰. 流动注射纳米金分光光度法快速测定乳制品中的三聚氰胺[J]. *分析实验室*, 2016, 35(8): 961-965.  
ZHAO J, LI YS, GAO XF. Flow injection nano-gold spectrophotometry for rapid determination of melamine in dairy products [J]. *Chin J Anal Lab*, 2016, 35(8): 961-965.
- [46] 陈俊峰, 贾敬亮, 张红彦. 酶联免疫法检测生乳中三聚氰胺的研究[J]. *中国乳业*, 2011, (8): 59-61.  
CHEN JF, JIA JL, ZHANG HY. Enzyme-linked immunoassay for the detection of melamine in raw milk [J]. *Chin Dairy Ind*, 2011, (8): 59-61.
- [47] HAN M, CONG L, WANG J, *et al.* An octuplex lateral flow immunoassay for rapid detection of antibiotic residues, aflatoxin M<sub>1</sub> and melamine in milk [J]. *Sens Actuat B Chem*, 2019, 292: 94-104.
- [48] WU KH, HUANG WC, CHANG SC, *et al.* Colloidal silver-based lateral flow immunoassay for rapid detection of melamine in milk and animal feed [J]. *Mater Chem Phys*, 2019, 231: 121-130.
- [49] LIAO X, CHEN C, SHI P, *et al.* Determination of melamine in milk based on  $\beta$ -cyclodextrin modified carbon nanoparticles via host-guest recognition [J]. *Food Chem*, 2020, 338. DOI: 10.1016/j.foodchem.2020.127769
- [50] MU WY, HUANG PZ, CHEN QY, *et al.* Determination of melamine and melamine-Cu(II) complexes in milk using a DNA-Ag hydrocolloid as the sensor [J]. *Food Chem*, 2019, 311. DOI: 10.1016/j.foodchem.2019.125889
- [51] JIGYASA, KAUR RJ. Bio-polyphenols promoted green synthesis of silver nanoparticles for facile and ultra-sensitive colorimetric detection of melamine in milk [J]. *Biosen Bioelectron*, 2018, 120: 153-159.

(责任编辑: 于梦娇)

#### 作者简介



祝海珍, 博士, 副教授, 主要研究方向为食品营养与卫生安全。  
E-mail: zhuhaizhen1979@sina.com