

基于钨丝原子阱与直接进样技术的 原子荧光光谱法快速测定贝类中的镉*

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摘要 本研究利用集成多孔石墨管电热蒸发器和钨丝捕获阱技术的原子荧光光谱分析系统,基于固体进样技术建立了适用于现场快速检测贝类中镉(Cd)的测定方法,实现了贝类中 Cd 的快速灵敏检测。结果显示,仪器在最佳参数条件下稳定性良好,采用“在线原子阱”捕获后释放的信号可以消除大多数基体干扰。贝类样品匀浆后在酸性条件下直接进样可快速测定 Cd,且使用 1%硝酸进样效果最好。采用标准曲线和标准加入法验证,均线性良好($R^2 \geq 0.995$),样品加标回收率分别为 98.1%–110.6%和 96.4%–105.5%,相对标准偏差(RSD)分别为 3.3%–11.6%和 7.5%–8.7%,方法检出限分别为 3 pg 和 0.6 pg,满足贝类样品的现场快速检测要求。但相对标准曲线法,标准加入法具有更好的准确度、精密度和稳定性,用标准物质验证,检测结果在参考值范围内。因此,标准加入法更适合贝类中 Cd 的快速测定。

关键词 固体进样; 原子荧光; 贝类; 镉; 测定

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镉(Cd)作为有毒有害重金属元素,一直是人们关注的重点。海洋生物对重金属有很强的富集作用,尤其是贝类体内 Cd 含量较高(吴春峰等, 2013; 崔正国等, 2015),是人体摄入 Cd 的重要来源之一。因此,监测环境及水产品中 Cd 的含量,是预防和减少 Cd 对人体危害的重要举措。目前,国际上 Cd 的检测方法已较为成熟,如原子吸收法(AAS)(Miranda *et al.*, 2012; 李立等, 2011)、原子荧光法(AFS)(Cava-Montesinos *et al.*, 2004; 王志嘉等, 2012)、电感耦合等离子体发射光谱和质谱法(ICP-AES/MS)(O'Sullivan *et al.*, 2013; 陈国娟, 2012; Juranović *et al.*,

2012)等,但均需繁琐的样品消解,难以实现现场及快速检测。直接进样分析是解决这一问题的有效手段,且已与多种检测方法结合并得到应用(Duarte *et al.*, 2013; 张英等, 2015; Bu *et al.*, 2013),然而,直接进样引入复杂基体所产生的干扰则需要用加入基体改进剂的方法来进行消除(叶佩琳等, 2015; Török *et al.*, 2012)。此外,也可以利用捕获技术来消除基体干扰,如 Feng 等(2010)利用钨丝“在线原子阱”实现了电热蒸出 Cd 的捕获,消除了基体干扰,并成功应用到了蔬菜、鸡肉等农产品中 Cd 的测定(Zhang *et al.*, 2012)。目前,电热蒸发钨丝在线捕获技术与光谱技术联用直

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接测定食品中的 Cd 含量在粮食、蔬菜、水果、茶叶、猪肝及干粉贝类中已有报道(Zhang *et al*, 2016; 冯礼等, 2014; Zhang *et al*, 2015; 黄亚涛等, 2013; 王昌钊等, 2012; Mao *et al*, 2013¹⁾; 毛雪飞, 2015)。而水产品由于含水量高、粘度大、基质复杂等特点, 在该方面的研究应用还较少(Wen *et al*, 2009; Yang *et al*, 2015)。

本研究应用集成多孔石墨管电热蒸发和钨丝捕获阱技术的固体进样测 Cd 装置串联原子荧光光谱分析系统, 针对贝类样品特点, 通过优化前处理方法, 确定最佳测定程序和条件, 建立了适用于现场快速检测贝类中 Cd 的测定方法, 旨在为贝类中 Cd 的现场快速检测提供一种有效技术手段。

1 材料与方法

1.1 材料

1.1.1 实验材料 扇贝、菲律宾蛤仔(*Ruditapes philippinarum*)、缢蛭(*Sinonovacula constricta*)等贝类样品(采集于山东青岛胶南地区); 扇贝标准物质 GBW10024(国家标准物质中心); 贻贝(*Mytilus edulis*)标准物质 GBW0857(国家海洋局第二海洋研究所); 牡蛎(*Ostrea gigas*)标准物质 ESA-2(中国环境监测总站); 其他验证试剂均为分析纯; 所用标准溶液均来自国家标准物质中心; 实验用水为超纯水; 载气及屏蔽气为 Ar-H₂ (9 : 1, V/V)混合气。

1.1.2 仪器设备 DCD-200 固体进样装置、AFS-8230 原子荧光光度计(北京吉天仪器有限公司); AA800 石墨炉原子吸收光度计(美国 Perkin-Elmer 公司); Milli-Q 超纯水(密理博公司); 微量移液器(德国 Eppendorf 公司); T18 均质机(德国 IKA 集团); 旋涡混匀器(德国 IKA 集团)。

1.2 实验方法

1.2.1 样品处理 取新鲜贝类可食部分用均质机处理, 称 20 mg 左右样品于进样舟中直接上机测量(视样品含量高低, 用 1%硝酸稀释上机)。

称取 1.00 g 标准物质用 1%硝酸稀释至 10 ml, 充分混匀, 吸取 20 μ l 于进样舟中上机测定。

1.2.2 标准曲线的制备 分别取 50 μ g/L Cd 标准溶液 0、2、4、6、8、10 μ l, 于石墨进样舟中测定其荧光值, 以进样 Cd 的绝对含量(ng)与测定荧光值绘制标准曲线。

1.2.3 标准加入法样品系列制备 取等量待测样品 1 ml 分装至 5 个试管中, 分别吸取 5 μ g/ml Cd 标准溶液 0、5、10、15、20 μ l 于相应管中(对应加标量分别为 0、25、50、75、100 ng), 用 1%硝酸稀释至 2 ml, 混匀, 制备加标样品系列。

1.2.4 测定方法 实验以 1%硝酸溶液作为空白, 进样 10 μ l 于样品舟中上机检测, 每个样品平行测定 3 次, 取平均值。

1.2.5 仪器条件 固体进样测 Cd 装置与电热蒸发原子荧光光谱仪联用(王昌钊等, 2012; 王金玉等, 2013), 原子荧光光谱仪工作参数见表 1。

用于方法验证的石墨炉原子吸收光谱仪(GF-AAS)仪器条件参考 GB/T5009.12-2003。

表 1 原子荧光光谱仪工作参数

Tab.1 The operating parameters of atomic fluorescence spectrometry (AFS)

| 参数 Parameters | 值 Value |
|--|------------|
| 灯电流 Lamp current (mA) | 20-100 |
| 光电倍增管负高压 Voltage for PMT (V) | -250-320 |
| 载气流速 Carrier gas flow rate (ml/min) | 500 |
| 屏蔽气流速 Shielding gas flow rate (ml/min) | 500 |
| 读数时间 Reading time (s) | 6 |

1.3 统计分析

采用 SPSS 18 统计软件进行 *t* 检验分析, 比较电热蒸发原子荧光法(ETV-AFS)和湿法消解法(GF-AAS)测定贝类样品中 Cd 含量结果的差异性。在 95%的置信度下, 如 $P > 0.05$, 则说明两种方法之间不存在显著性差异。

2 结果与讨论

2.1 固体进样装置参数优化

根据设备操作相关信息, 通过添加 0.1 ng Cd 标准溶液, 对灰化功率、灰化时间、蒸发功率、蒸发时间进行四因素三水平的正交实验, 研究灰化和蒸发功率及时间对测定的影响。结果以测定的荧光响应值面积为判定依据, 重复测定 3 次的相对标准偏差 RSD 值作为参考。温控程序的正交实验设计和结果分别如表 2、表 3 所示。

1) Mao XF. Study on Determination of cadmium and mercury in agri-foods by solid sampling electrothermal vaporization spectrometry using atomic traps. Doctoral Dissertation of Chinese Academy of Agricultural Sciences, 2015 [毛雪飞. 固体进样电热蒸发原子阱捕获光谱技术快速测定农产品中镉和汞的研究. 中国农业科学院博士研究生学位论文, 2015]

表2 温度程序正交实验设计

Tab.2 The orthogonal experimental design of temperature programs

| 水平 Level | A 灰化功率 Ashing power(W) | B 灰化时间 Ashing time (s) | C 蒸发功率 Vaporization power(W) | D 蒸发时间 Vaporization time(s) |
|-------------|---------------------------|---------------------------|---------------------------------|--------------------------------|
| 1 | 50 | 30 | 60 | 20 |
| 2 | 70 | 50 | 70 | 30 |
| 3 | 100 | 70 | 80 | 40 |

由正交实验 $L_9(3^4)$ (表3)可知, $R_C > R_D > R_A > R_B$, 说明 C 因素影响最大, 其次为 D、A、B 因素, 影响逐渐变小, 即固体进样温控程序中影响测定结果的程序因素依次为蒸发功率>蒸发时间>灰化功率>灰化时间, 根据 Cd 因素指标趋势得出最佳温控程序组合为 $C_3D_3A_3B_2$ 。因此, 实验最终确定灰化功率为 100 W, 灰化时间为 50 s, 蒸发功率为 80 W, 蒸发时间为 40 s。按照最佳条件进行验证实验(表4), 重复 3 次, 测得荧光面积为 $5.8 \times 10^5 \text{ mV} \cdot \text{s}$, RSD 为 3.7%。

表3 温度程序控制的正交实验结果

Tab.3 Orthogonal experimental results of temperature programs

| 实验号 No. | 灰化功率 Ashing power (W) | 灰化时间 Ashing time (s) | 蒸发功率 Vaporization power (W) | 蒸发时间 Vaporization time (s) | 荧光面积 Fluorescent area (mV·s) | RSD(%) |
|------------|--------------------------|-------------------------|--------------------------------|-------------------------------|---------------------------------|--------|
| 1 | 1(50) | 1(30) | 1(60) | 1(20) | 3.17 | 7.9 |
| 2 | 1 | 2(50) | 2(70) | 2(30) | 4.27 | 2.4 |
| 3 | 1 | 3(70) | 3(80) | 3(40) | 4.89 | 2.2 |
| 4 | 2(70) | 1 | 2 | 3 | 4.91 | 2.1 |
| 5 | 2 | 2 | 3 | 1 | 5.29 | 2.8 |
| 6 | 2 | 3 | 1 | 2 | 3.65 | 3.0 |
| 7 | 3(100) | 1 | 3 | 2 | 6.05 | 2.8 |
| 8 | 3 | 2 | 1 | 3 | 4.60 | 3.0 |
| 9 | 3 | 3 | 2 | 1 | 3.68 | 3.9 |
| K_1 | 12.33 | 14.13 | 11.42 | 12.14 | | |
| K_2 | 13.90 | 14.20 | 12.90 | 13.98 | | |
| K_3 | 14.30 | 12.20 | 16.20 | 14.40 | | |
| k_1 | 4.11 | 4.71 | 3.81 | 4.05 | | |
| k_2 | 4.62 | 4.72 | 4.29 | 4.66 | | |
| k_3 | 4.78 | 4.08 | 5.41 | 4.80 | | |
| R | 0.67 | 0.63 | 1.60 | 0.75 | | |

表4 固体进样装置分析过程

Tab.4 Analytical procedures of the solid sampling device

| 程序 Programs | 时间 Time (s) | 功率 Power (W) | 信号采集 Signal acquisition |
|-------------------------------|----------------|-----------------|----------------------------|
| (1)灰化 Ashing | 30.0 | 70.0 | 否 No |
| (2)灰化 Ashing | 20.0 | 100.0 | 否 No |
| (3)蒸发/捕获 Vaporization/trap | 35.0 | 80.0 | 否 No |
| (4)蒸发/捕获 Vaporization/trap | 5.0 | 0.0 | 否 No |
| (5)释放 Release | 1.0 | 50.0 | 是 Yes |
| (6)释放 Release | 5.0 | 0.0 | 是 Yes |
| (7)蒸发 Vaporization | 4.0 | 260.0 | 否 No |
| (8)冷却 Cooling | 5.0 | 0.0 | 否 No |
| (9)清除 Cleaning | 1.0 | 50.0 | 否 No |
| (10)冷却 Cooling | 5.0 | 0.0 | 否 No |

2.2 仪器稳定性实验

实验在最优条件下添加不同 Cd 标准溶液的多谱图如图 1 所示。仪器在最适条件下, 8 h 内每隔 1 h 测量 1 次, 每次平行测定 3 次, 其测量值的相对标准偏差(RSD)为 7.41%。测量含 Cd 0.1 ng 的 RSD 小于 10%, 测定稳定性较好。

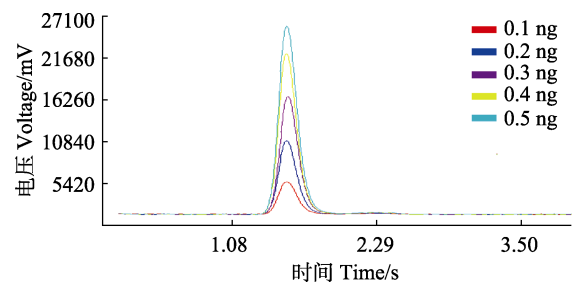


图1 标准溶液光谱

Fig.1 The spectrogram of standard solutions

2.3 干扰实验

基于鲜贝样品基体成分特点(李莘莘, 2014; 俞佳锋等, 2014), 实验以 1 ng Cd 为基准, 通过添加一定量的有机成分(葡萄糖、蛋白胨、琼脂等用于验证糖

类、蛋白等主要组分)和无机元素(Ca、Na、Zn、Se、Al、Pb、Hg、As 等样品中的主要元素), 验证基体干扰情况。实验结果如表 5 所示, 除 NaCl 干扰较大外, Cd 回收率($n=3$)在 99.3%–110.8%, 干扰不显著。

表 5 干扰物对测量的影响
Tab.5 The interferences of inorganic and organic materials

| 干扰物 Interferents | 浓度 Concentration (mg/L) | 回收率 Recovery (%) | 干扰物 Interferents | 浓度 Concentration (mg/L) | 回收率 Recovery (%) |
|----------------------|----------------------------|---------------------|---------------------|----------------------------|---------------------|
| 葡萄糖 Glucose | 10000 | 102.2 | As | 20 | 109.2 |
| 琼脂 Agar | 10000 | 105.6 | Zn | 30 | 107.1 |
| 胰蛋白胨 Casein tryptone | 100000 | 99.6 | Se | 10 | 107.5 |
| 葡聚糖 Glucan | 5000 | 100.2 | Al | 50 | 109.7 |
| NaCl | 20000 | 87.4 | Pb | 20 | 99.3 |
| Ca | 80 | 110.6 | Hg | 20 | 110.8 |

2.4 酸溶液对检测的影响

贝类样品Cd含量较高且基体成分复杂, 为保证实验测量精确度, 需将样品稀释, 同时为减少可能的干扰, 通过稀释减少基体对测量的影响。研究发现, 酸性条件有助于分解有机物、降低干扰。实验研究了常用的酸, 包括硝酸、盐酸、高氯酸和硫酸, 发现同浓度的硝酸介质在测定试样时荧光响应值及稳定性优于盐酸、硫酸和高氯酸(图2)。进一步研究表明, 样品加入1%硝酸效果较好, 如图3所示。因此, 本方法选择1%硝酸作为样品稀释液。

2.5 标准曲线

Cd 元素测定的常规方法是标准溶液曲线法(Shai *et al*, 1994), 但对于固体进样方式, 标准加入法是消除基质干扰的有效方法之一, 因此应用更多(Pouny *et al*, 1992)。本研究采用扇贝标准物质作为基质添加标准溶液进行验证, 两者无显著差异。图 4、图 5 分别为标准溶液拟合标准曲线及扇贝标准物质的标准加入法拟合曲线, $R^2>0.995$, 相关性较好。

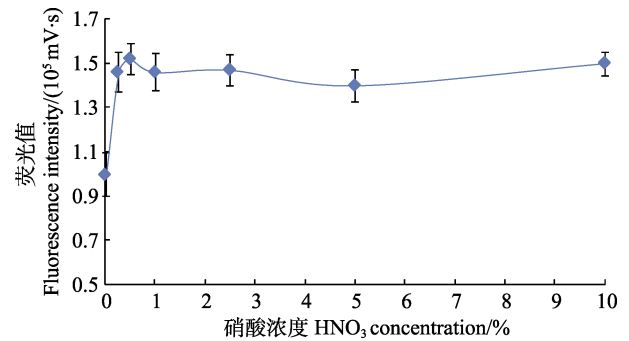


图 3 硝酸浓度对荧光值的影响
Fig.3 The effect of HNO₃ concentration on fluorescence intensity

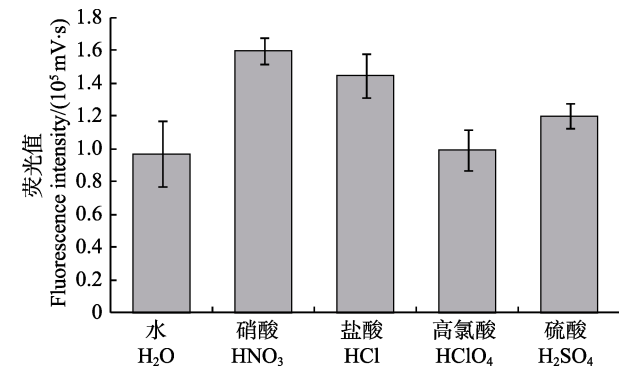


图 2 不同酸条件下的荧光值
Fig.2 Fluorescence intensities in different acid solutions

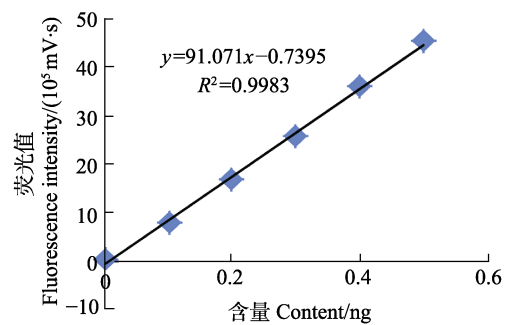


图 4 标准曲线法拟合曲线
Fig.4 The fitting curves of standard curve method

2.6 方法验证

2.6.1 方法稳定性和灵敏度 室温条件下, 仪器在 10 h 内每隔 1 h 测量 1 次($n=3$), 其 RSD 为 8.4%, 说明仪器稳定性良好; 对同一样品连续测定 6 次, 其 RSD 在 6.1%–12.1%之间。按 IUPAC 标准, 以 0.2 $\mu\text{g/L}$ Cd 标准溶液($n=20$)测得标准加入法和标准曲线法的方法检测限分别为 0.6 pg 和 3 pg。

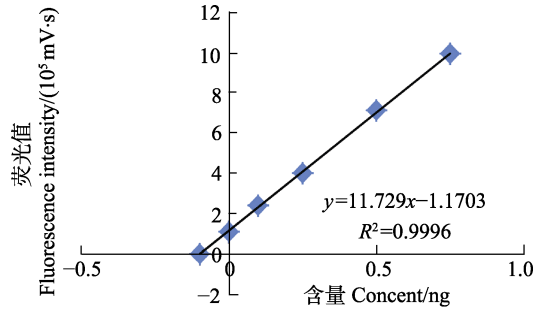


图5 标准加入法拟合曲线

Fig.5 The fitting curves of standard addition method

2.6.2 加标回收实验 对于菲律宾蛤仔和扇贝样品分别添加一定量的Cd进行加标回收实验($n=3$),结果显示(表6),标准加入法加标回收率在96.4%–105.5%之间,RSD在6.5%–7.7%之间;标准曲线法加标回收率在98.1%–110.6%之间,RSD在3.3%–8.6%之间。说明标准加入法的准确度、精密度要优于标准曲线法。

2.6.3 标准物质验证 由表7($n=3$)可以看出,标准曲线法测定标准物质中Cd含量与标准参考值相差较大,准确度低;而用标准加入法测定的标准物质Cd含量在标准参考值范围内,准确度较高。

表6 不同测定方法的加标回收结果

Tab.6 Recoveries of spiked Cd using different methods

| 方法 Methods | 样品 Samples | 加标量 Spiked (mg/kg) | 回收率 Recovery (%) | RSD (%) |
|-----------------------------------|---|--------------------|------------------|---------|
| 标准曲线法 Standard curve method | 菲律宾蛤仔 <i>Ruditapes philippinarum</i> | 0.5 | 98.1 | 6.3 |
| | 扇贝 Scallop | 1 | 102.2 | 8.2 |
| | | 2 | 103.7 | 3.3 |
| | | 2 | 110.9 | 7.1 |
| 标准加入法 Standard addition method | 菲律宾蛤仔 <i>Ruditapes philippinarum</i> | 3 | 105.5 | 7.9 |
| | 扇贝 Scallop | 5 | 110.6 | 8.6 |
| | | 1 | 96.4 | 7.7 |
| | | 2 | 105.5 | 6.5 |

表7 不同方法标准物质验证结果

Tab.7 Validation of Cd measurements using different methods

| 方法 Methods | 有证标准物质 Certified reference materials | 标物编号 Number | 测定值 Measured value (mg/kg) | 标准参考值 Certified value (mg/kg) |
|-----------------------------------|---|----------------|-------------------------------|----------------------------------|
| 标准曲线法 Standard curve method | 扇贝 Scallop | GBW10024 | 0.93±0.05 | 1.06±0.10 |
| | 贻贝 Mussel | GBW0857 | 4.95±0.03 | 4.50±0.30 |
| | 牡蛎 Oyster | ESA-2 | 5.21±0.07 | 4.56±0.48 |
| 标准加入法 Standard addition method | 扇贝 Scallop | GBW10024 | 1.12±0.02 | 1.06±0.10 |
| | 贻贝 Mussel | GBW0857 | 4.44±0.05 | 4.50±0.30 |
| | 牡蛎 Oyster | ESA-2 | 4.59±0.01 | 4.56±0.48 |

2.6.4 实际样品检测 对于扇贝、菲律宾蛤仔、缢蛏等贝类样品,应用标准加入法ETV-AFS与GF-AAS法进行比较(表8),方差分析显示,检测结果无显著性差异($P>0.05$)。

表8 ETV-AFS与GF-AAS测定值对比

Tab.8 Comparison of ETV-AFSA and GF-AAS determinations ($n=3$)

| 样品编号 Sample No. | 测定值 Measured value(mg/kg) | |
|--------------------|---------------------------|------------|
| | ETV-AFS | GF-AAS |
| 1 | 3.527±0.52 | 3.461±0.09 |
| 2 | 2.973±0.49 | 2.823±0.05 |
| 3 | 0.288±0.11 | 0.281±0.01 |
| 4 | 0.101±0.05 | 0.095±0.01 |
| 5 | 0.135±0.05 | 0.127±0.02 |

3 结论

本研究确定了利用钨丝在线捕获的电热蒸发原子荧光光谱法测定贝类中Cd的最佳仪器条件,建立了适用于现场快速检测的Cd检测方法,可快速准确测定不同贝类样品中的Cd含量。研究发现,标准加入法和标准曲线法均能满足现场小批量检测的要求,样品前处理的分析时间可以控制在5 min之内,方法检出限分别为0.6 pg和3 pg。相对于标准曲线法,标准加入法具有更好的测定准确度和重现性,因此,建议采用标准加入法进行贝类中Cd的快速检测。

本方法无需消解,操作简便,检验时间短,可实现小批量样品的现场快速检测,为产地准出和市场准入提供了一种有效手段。

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Rapid Determination of Cadmium in Shellfish Based on Direct Sampling Electrothermal Vaporization Atomic Fluorescence Spectrometry with a Tungsten Coil Trap

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Abstract Cadmium is among the most toxic metals in the aquatic environment. It particularly affects shellfish because the latter can accumulate large amounts of cadmium from the water. To reduce the potential risk on the health of public consumers, it is necessary to measure and monitor the level of cadmium in shellfish. Conventional analysis methods are usually time-consuming due to the prolonged sample digestion and pretreatments. A direct solid sampling technology without digestion treatment has been applied in the fast determination of cadmium concentration in agricultural produces such as grains and vegetables. Here, we tried to employ this method in the rapid measurement of cadmium concentration in shellfish. Solid sampling (SS) device was coupled with atomic fluorescence spectrometry (AFS), and the SS-AFS instrument was assembled with a tungsten coil trap (TCT) and porous carbon ETV. Meanwhile, electrothermal vaporization atomic fluorescence spectrometry (ETV-AFS) with a tungsten coil trap was optimized, and SS-ETV-AFS was established as a novel direct sampling method of detecting cadmium in shellfish. The results showed that a tungsten coil could work as a cadmium trap and eliminate most of the matrix interferences. Samples were homogenized and diluted with different acids, and 1% HNO₃ was determined to be the optimal acid reagent. Under the optimized conditions, the fitting with both the standard addition method and the standard curve method showed good linearity with regression coefficient (R^2) larger than 0.995. The relative standard deviation (RSD) of the standard addition method and the standard curve method were 6.5%–7.7% and 3.3%–8.6% respectively; the spiked recoveries of them were 96.4%–105.5% and 98.1%–110.6%; the limit of detection (LOD) were 0.6 pg and 3 pg. Moreover, the time elapsed (including sample pretreatments) was within 5 min. The standard addition method generated data with similar accuracy to those measured with graphite furnace atomic absorption spectrophotometry (GFAAS) or certified reference materials (CRMs) ($P > 0.05$). Therefore, the standard addition method could be suitable to the field analysis and monitoring of cadmium in shellfish.

Key words Solid sampling; Atomic fluorescence spectrometry; Shellfish; Cadmium; Determination

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