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半流动薄层电解池-吸附伏安法的研究及其
在鱼肉氯霉素残留快速检测中的应用

Adsorptive Stripping Voltammetry in a Flow-through Thin Layer
Cell for the Determination of Chloramphenicol in Fish Meats

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**Adsorptive Stripping Voltammetry in a Flow-through Thin Layer
Cell for the Determination of Chloramphenicol in Fish Meats**

**A Dissertation Submitted for
the Degree of Master of Science**

by

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摘要

论文研制了一种半流动薄层电解池,该电解池采用玻碳为工作电极,对玻碳电极表面活化过程和活化后的玻碳电极对氯霉素的吸附作用进行了研究,建立了半流动薄层吸附伏安法,并成功地将该方法用于鱼肉氯霉素残留的快速检测。

本论文共分四章。

第一章分别介绍了薄层电化学和吸附伏安法的原理、特点、应用以及氯霉素的各种检测方法,提出本文研究半流动薄层吸附伏安法并将其用于鱼肉中氯霉素残留快速检测的技术路线和创新意义。

第二章介绍了所研制的半流动薄层电解池,利用该电解池对氯霉素在更宽电位范围(相对于汞电极)内的电化学行为进行了初步探讨,并研究了薄层池的结构(电极面积、薄层厚度)对氯霉素伏安行为的影响。

第三章分为两节:第一节考察了采用不同的电化学方法对玻碳电极表面进行活化后,电极表面的形态和对氯霉素的吸附效果。第二节对几种可能对氯霉素的吸附和检测造成影响的因素进行实验和比较,确立了最佳的氯霉素测定参数。

第四章分为两节:第一节建立了高效液相色谱法用于鱼肉中氯霉素残留的检测方法。该方法具有较好的线性关系和较高的加标回收率,可作为标准方法。第二节建立了以玻碳电极为工作电极的半流动薄层池用于鱼肉中氯霉素残留快速检测的方法。测定氯霉素的线性范围为 9~9500ng/mL,相关系数 $R^2=0.998$;方法检测限为 1.5 $\mu\text{g}/\text{kg}$ 氯霉素;实际样品平行测定重现性 $\text{RSD}=2.2\sim 16\%$ (3个样品每次各重复测定3次),不同次测定重现性 $\text{RSD}=2.5\sim 3.4\%$ (3个样品重复测定2~3次)。5种不同鱼类样品加标(加标量为 7.5~30 $\mu\text{g}/\text{kg}$)回收率为 33.6~97.6%,平均回收率为 58.6%。本方法测得的结果与用高效液相色谱法测得的结果基本符合。

本研究课题的创新性在于:

1. 研制了一种池体积小,工作电极表面积大,方便拆卸、清洗的半流动薄层电解池;该薄层池的辅助电极、参比电极与工作电极采用面对面排布,提高电流效率,降低溶液电阻降;采用半流动工作模式:即进样时流动,检测时静止,既易于更换被测溶液,又保证检测时处于扩散传质过程。

2. 对氯霉素在更宽电位范围（相对于汞电极）内的电化学反应进行了初步探讨。

3. 首次利用经电化学活化处理后的玻碳电极对氯霉素有吸附作用的特点来提高对氯霉素的检测灵敏度。系统考察了采用不同电化学方法活化后的玻碳电极对氯霉素的吸附效果，研究了可能对氯霉素检测结果产生影响的各种因素。

4. 首次成功地将以玻碳电极为工作电极的半流动薄层电解池与吸附伏安法相结合用于鱼肉氯霉素残留的快速检测。

5. 对鱼肉样品的前处理方法进行摸索，确立了适合本方法又简单的样品前处理步骤。

关键词：半流动；薄层电解池；吸附伏安法；鱼；氯霉素

Abstract

A flow-through thin layer cell is designed and fabricated. A rapid and sensitive method, based on the adsorptive accumulation of chloramphenicol at the electrochemically pretreated glassy carbon electrode in the above mentioned thin layer cell, for determination of chloramphenicol residues in fish meats has been developed.

Chapter one presents a brief overview of thin layer electrochemistry, adsorptive stripping voltammetry and methods for determination of chloramphenicol residues. The innovation of the study is also addressed.

Chapter two deals with design of a flow-through thin layer cell. Electrochemical behavior of chloramphenicol over a broad range of voltage was studied. Also studied was electrolysis of chloramphenicol in the thin layer cell that employs electrodes of different surface area at different thickness and in a common electrochemical cell.

Chapter three was aimed at electrochemical pretreatment of glassy carbon electrodes in the thin layer cell and adsorption of chloramphenicol at pretreated electrodes. Different chemical and electrochemical variables in the pretreatment step were optimized and the surfaces of the glassy carbon electrodes before and after pretreatment were examined by scanning electron microscopy (SEM). Optimum conditions for adsorbing and then determining chloramphenicol were investigated.

Chapter four was aimed at development of a new and rapid method for determination of chloramphenicol residues in fish meats as well as identification of chloramphenicol in positive samples by HPLC. The new method is based on the adsorptive accumulation of chloramphenicol at the electrochemically pretreated glassy carbon electrode in the thin layer cell. Calibration graphs were linear ($R^2=0.998$) in the 9 to 9500ng/mL concentration range. A limit of detection of 1.5 μ g/kg was found. The repeatability and reproducibility were 2.2~16% and 2.5~3.4% respectively. The recoveries of chloramphenicol from five kinds of fish meats spiked at 7.5~30 μ g/kg were 33.6~97.6%. A simple HPLC method with a limit of detection of about 8 μ g/kg has been developed for identification of chloramphenicol in

positive samples. There is an excellent correlation between the results obtained with the adsorptive stripping voltammetry in the thin layer cell and the HPLC method.

The innovation of the study is as follows:

1. A simple and convenient flow-through thin layer cell has been designed, which employs a large area glassy carbon electrode and is easy to fabricate. The working electrode is placed face to face against the auxiliary and reference electrode to lower the resistance of the solution and improve the performance of the thin layer cell. It is convenient to renew the solution and the electrode surface in the thin layer cell since the flow pattern is adopted.

2. Electrochemical behavior of chloramphenicol over a broad range of voltage was studied.

3. The voltammetry of chloramphenicol at glassy carbon electrodes was improved on the basis of the adsorption of chloramphenicol at the electrodes pretreated electrochemically. Different chemical and electrochemical variables in the pretreatment step as well as conditions for adsorbing and determining chloramphenicol were optimized.

4. The adsorptive stripping voltammetry in a flow-through thin layer cell was applied to the rapid determination of chloramphenicol in fish meats for the first time.

5. A simple extraction procedure was set up.

Keywords: Flow-through; Thin layer cell; Adsorptive stripping voltammetry; Fish; Chloramphenicol

第一章 前言^[1~3]

1.1 薄层电化学

薄层电解池首先在二十世纪 60 年代初期得到利用。它将很小的溶液体积（几个 μL ）限制在电极表面的一个薄层内（ $2\sim 100\mu\text{m}$ ），通过减少测定液体积来增大电极表面积与测定液体积比 A/V ，这样只需很短的时间就能将样品完全电解。

1.1.1 薄层电解池的结构

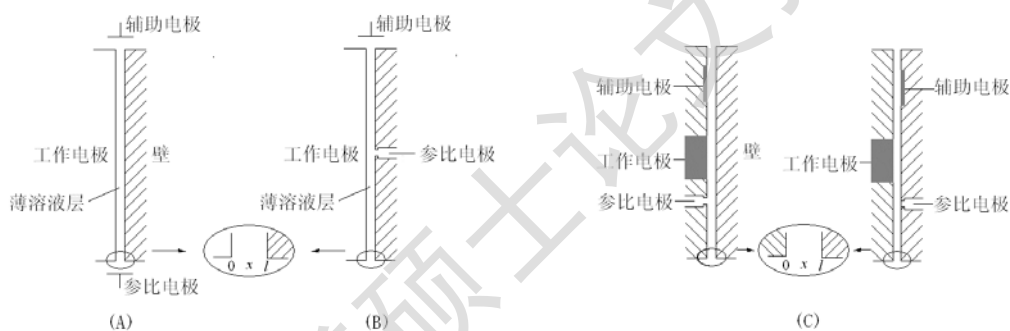


图 1-1 薄层电解池示意图

Fig. 1-1 Schematic diagrams of thin layer electrochemical cells.

图 1-1 所示为薄层电解池示意图。早期报导的薄层池 (A) 的薄层室中只有工作电极，参比和辅助电极放在薄层室之外，这种设计的不利之处在于：由于参比和辅助电极放在薄层室外，会有严重的不均匀电流分布和高的未补偿 iR 降（例如会导致非线性电势扫描）^[4]。后来，研究者对薄层池的结构作了改进，将工作电极和参比电极放在薄层室内，辅助电极放在薄层室外 (B) ^[5,6]，这样可消除前一种结构带来的不利影响。另一种类型是工作、参比和辅助电极均放在薄层室内 (C)，设计这种类型的薄层池时要注意保持辅助电极与工作电极之间有一定距离，以避免两个扩散层之间的干扰，同时尽量使参比电极靠近工作电极^[7]。

1.1.2 薄层电化学理论

当薄层池的厚度 l 在给定的实验时间内小于扩散层的厚度，即 $l \ll (2Dt)^{1/2}$ ，或者说

薄层电解池的厚度 l 固定时，在低扫描速度下，薄层池循环伏安行为与耗竭性薄层池电流公式相符，

$$i_p = \frac{n^2 F^2 \nu C^*}{4RT} \quad \text{可逆反应}$$

$$i_p = \frac{n\alpha n_a F^2 \nu C^*}{2.718RT} \quad \text{不可逆反应}$$

图 1-2 为典型的薄层电解池中扫描伏安图（可逆反应）^[8]，图 1-3 为不可逆过程在薄层池中的线性扫描伏安图。

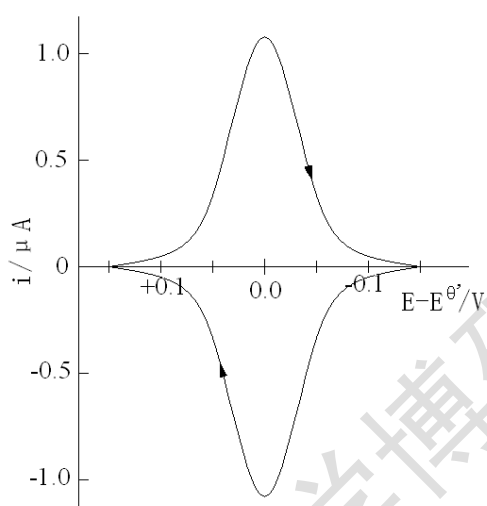


图 1-2 耗竭性薄层池的循环伏安图
(可逆反应)

Fig. 1-2 Thin layer cyclic voltammogram of the reversible reaction.

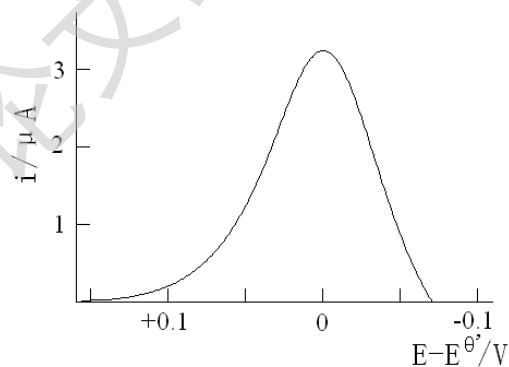


图 1-3 不可逆过程在薄层池中的线性扫描伏安图

Fig. 1-3 Thin layer stripping voltammogram of the irreversible reaction.

高扫描速度下，其循环伏安行为与半无限扩散理论^[9,10]相符，

$$i_p = 0.4463 \frac{n^{\frac{3}{2}} F^{\frac{3}{2}}}{R^{\frac{1}{2}} T^{\frac{1}{2}}} A D^{\frac{1}{2}} \nu^{\frac{1}{2}} C^* \quad \text{可逆反应}$$

$$i_p = 0.4958 \frac{\alpha n^{\frac{3}{2}} F^{\frac{3}{2}}}{R^{\frac{1}{2}} T^{\frac{1}{2}}} D^{\frac{1}{2}} \nu^{\frac{1}{2}} A C^* \quad \text{不可逆反应}$$

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