

**Universidade de São Paulo
Escola Superior de Agricultura “Luiz de Queiroz”**

Microextração sólido-líquido para diotiocarbamatos em alimentos *in natura*

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Dissertação apresentada para obtenção do título de Mestra em Ciências. Área de concentração: Ciência e Tecnologia de Alimentos

**Piracicaba
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Engenheira de Alimentos

Microextração sólido-líquido para diotiocarbamatos em alimentos *in natura*
versão revisada de acordo com a resolução CoPGr 6018 de 2011

Orientadora:
Profa. Dra. WANESSA MELCHERT MATTOS

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*“Quando se sonha sozinho é apenas um sonho.
Quando se sonha juntos é o começo da realidade.”*

Miguel de Cervantes

RESUMO

Microextração sólido-líquido para ditiocarbamatos em alimentos *in natura*

Os ditiocarbamatos têm sido bastante empregados nas práticas agrícolas em razão da eficiência em evitar/controlar pragas, e também devido à baixa toxicidade e instabilidade quando comparados com outros pesticidas. Entretanto, esta classe pode proporcionar alguns efeitos adversos para a saúde humana, necessitando do controle em amostras de alimentos. Este trabalho foi dividido em dois capítulos, no primeiro, revisão bibliográfica detalhada foi realizada para as microextrações de fase sólida e líquida de pesticidas carbamatos e ditiocarbamatos em amostras de alimentos. Vantagens e desvantagens, aplicações, comparações com os métodos tradicionais de preparo de amostras e discussões dos parâmetros analíticos foram exploradas ao longo do texto. No segundo capítulo, foi desenvolvido laboratorialmente uma metodologia de microextração de manebe de alimentos *in natura*. Para tanto, foi explorada microextração sólido-líquido com determinação indireta de manebe por espectroscopia de absorção atômica de chama com injeção em fluxo. Resposta linear foi observada entre 0,9 a 20,0 $\mu\text{mol L}^{-1}$ de manebe, boa repetibilidade (4,0%) e reprodutibilidade (3,4%), limites de quantificação (6,0 $\mu\text{mol L}^{-1}$) e detecção (0,20 $\mu\text{mol L}^{-1}$), abaixo do estabelecido pelos órgãos reguladores. A extração do manebe foi realizada com 685 μL da solução $1,0 \times 10^{-3} \text{ mol L}^{-1}$ de EDTA, e apresenta excelentes valores de recuperação de 86 a 103%. A metodologia desenvolvida é uma alternativa ambientalmente amigável para a extração de manebe de amostras de alimentos (maçã, mamão e tomate) e não é influenciada pela degradação do composto alvo.

Palavras-chave: Manebe, Microextração sólido-líquido, Alimentos, Espectroscopia de absorção atômica de chama

ABSTRACT

Solid-liquid microextraction to dithiocarbamates in natura foods

Dithiocarbamates have been widely used in agricultural practices due to their efficiency in avoiding and/or controlling pests, and also by low toxicity and instability compared to other pesticides. Nonetheless, this class can provoke some adverse effects on human health, needing the determination of them in the food samples. This work was divided into two chapters, in the first, a detailed bibliographic review was made for solid-phase and liquid-phase microextractions of the carbamates and dithiocarbamates in food samples. The advantages, disadvantages, applications, comparisons with traditional methods, and discussions of the analytical parameters were explored throughout it. In the second chapter, it was developed laboratory a microextraction methodology for the extraction of maneb natura foods. Therefore, it was explored the solid-liquid phase microextraction for maneb with posterior indirect determination by flow injection analysis-flame absorption atomic spectroscopy. The linear range was from 0.9 to 20.0 $\mu\text{mol L}^{-1}$ of maneb, good repeatability (4.0%) and reproducibility (3.4%), detection (0.20 $\mu\text{mol L}^{-1}$), and quantification (6.0 $\mu\text{mol L}^{-1}$) limit, below of the established by regulatory agencies. The extraction of maneb was made using 685 μL of solution of the 1.0×10^{-3} mol L^{-1} of EDTA and showed excellent recovery from 86 to 103%. This microextraction demonstrated be an alternative environmentally friendly for the maneb extraction from foodstuffs (apple, papaya, and tomato), and it was not influenced by degradation of it.

Keywords: Maneb, Solid-liquid phase microextraction, Foods, Flame atomic absorption spectroscopic

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1. CONTEXTUALIZAÇÃO

Os ditiocarbamatos é uma classe bastante empregada nas práticas agrícolas em razão da baixa toxicidade e ampla aplicabilidade no controle de fungos e outras pragas. Além disto, esta classe é especial quando comparada com as outras devido ao emprego dos compostos na área industrial, práticas agrícolas e também na medicina. Isto ocorre por causa dos diferentes níveis de toxicidade, quando ingeridos inadequadamente acima da Nível Sem Efeitos Adversos Observáveis (NOAEL, do inglês No Observed Adverse Effect Level) podem provocar efeitos adversos à saúde humana. Agências regulamentadoras de cada país e o *Codex Alimentarius* estabelecem limites máximos de resíduos destes pesticidas em água e alimentos.

O desenvolvimento de metodologias para determinação dos ditiocarbamatos de forma seletiva e sensível é fundamental. No entanto, a composição das amostras podem influenciar diretamente no resultado analítico devido aos efeitos dos interferentes, sendo necessárias etapas de preparo de amostra, para minimizar/eliminar os efeitos de matriz. Estas etapas, geralmente, empregam grandes quantidades de solventes orgânicos e são muito morosas, promovendo erros sistemáticos e até mesmo contaminações. Alternativamente podem ser utilizadas na extração dos ditiocarmatos as microextrações de fase sólida e líquida, as quais são baseadas nas metodologias tradicionais de extração de fase sólida e extração líquido-líquido, respectivamente.

A dissertação apresentada é focada nos pesticidas ditiocarbamatos e em uma alternativa de extração ambientalmente mais amigável. O trabalho foi dividido em dois capítulos, no primeiro, revisão bibliográfica detalhada foi realizada para as microextrações de fase sólida e líquida para a extração de pesticidas carbamatos em amostras de alimentos. Vantagens e desvantagens, aplicações, comparações com os métodos tradicionais de preparo de amostras e discussões dos parâmetros analíticos foram exploradas ao longo do texto. No segundo capítulo, foi desenvolvido laboratorialmente uma metodologia de microextração de manebe de alimentos *in natura*. Para tanto, foi explorada microextração sólido-líquido com determinação indireta de manebe por espectroscopia de absorção atômica de chama com injeção em fluxo.

2. CONCLUSÃO GERAL

Os ditiocarbamatos são bastante empregados nas práticas agrícolas no Brasil, mesmo apresentando altos níveis de toxicidade e sendo proibidos na União Europeia e nos Estados Unidos. A determinação em amostras de alimentos e água é fundamental para controlar a concentração dos pesticidas ditiocarbamatos. No entanto, estas amostras possuem alto grau de complexidade podendo interferir nas análises, necessitando da realização de etapas de preparo de amostra para aumentar a sensibilidade e seletividade. Assim, nesta dissertação foi mostrado as principais microextrações de fase sólida e líquida empregadas nas extrações de ditiocarbamatos, as aplicações, vantagens, desvantagens e os parâmetros analíticos das metodologias de análises.

O desenvolvimento de uma metodologia de microextração sólido-líquida, rápida, simples e de baixo custo de manejo de amostras de alimentos foi realizado. Algumas vantagens foram alcançadas como os resultados analíticos não serem influenciados pela degradação do pesticida, a alta frequência analítica, e a não utilização de solvente orgânico, conferindo uma metodologia amigável ao meio ambiente e ao ser humano. Além disso, excelentes valores de precisão, exatidão e sensibilidade foram estimados, os quais foram avaliados de acordo com repetibilidade (4,0%), reprodutibilidade (3,4%), recuperação (86 - 103 %) e limite de detecção ($0,20 \mu\text{mol L}^{-1}$).

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Chapter 1

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