



# Multiclass detection and quantitation of antibiotics and veterinary drugs in shrimps by fast liquid chromatography time-of-flight mass spectrometry

Marina Villar-Pulido, Bienvenida Gilbert-López, Juan F. García-Reyes, Natividad Ramos Martos, Antonio Molina-Díaz\*

Analytical Chemistry Research Group (FQM-323), Department of Physical and Analytical Chemistry, University of Jaén, Campus Las Lagunillas, Edificio B-3, 23071 Jaén, Spain

## ARTICLE INFO

### Article history:

Received 12 April 2011

Received in revised form 1 June 2011

Accepted 11 June 2011

Available online 17 June 2011

### Keywords:

Multiresidue

Antibiotics

Shrimps

Seafood

Liquid chromatography

Mass spectrometry

## ABSTRACT

A fast liquid chromatography time-of-flight mass spectrometry (LC–TOFMS) method has been developed for simultaneous quantitative multiclass determination of residues of selected antibiotics and other veterinary drugs (benzalkonium chloride, ethoxyquin, leucomalachite green (LMG), malachite green (MG), mebendazole, sulfadiazine, sulfadimethoxine, sulfamethazine, sulfamethizole, sulfanilamide, sulfapyridine, sulfathiazole and trimethoprim) in shrimps. Different sample treatment methodologies were tested for the extraction of the targeted species based on either liquid partitioning with different solvents, solid-phase extraction or and matrix solid-phase dispersion. The final selected extraction method consisted of solid–liquid extraction protocol using acetonitrile as solvent followed by a clean-up step with primary secondary amine (QuEChERS). Recovery rates for the extraction of the selected multiclass chemicals were in the range 58–133%. Subsequent identification, confirmation and quantitation were carried out by LC–TOFMS analysis using a reverse-phase C<sub>18</sub> column with 1.8 μm particle size. The confirmation of the target species was based on accurate mass measurements of the protonated molecules ([M+H]<sup>+</sup>) and their fragment ions, obtaining routine accuracy errors lower than 2 ppm in most cases. The optimized LC–TOFMS method displayed excellent sensitivity for the studied analytes, with limits of detection (LODs) in the range 0.06–7 μg kg<sup>-1</sup>. Finally, the proposed method was successfully applied to the analysis of 12 shrimp samples collected from different supermarkets, showing the potential applicability of the method for ultratrace detection of these chemicals in such complex matrix.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The use of veterinary drugs in food production has been an issue of increasing concern for consumers during the last years. For instance, the intensive use of chemotherapeutic agents to treat infectious diseases in aquaculture has led to a frequent occurrence of drug-resistant microorganisms (including multiple-antibiotic resistant bacteria). In fact, in Europe there are currently in force some regulations establishing maximum residue levels (MRLs) for various antibiotics in fish [1,2], including, among others, sulfonamides, tetracyclines and emamectin. Other veterinary drugs (e.g. malachite green (MG) and its main metabolite, leucomalachite green (LMG)) are not authorized for use in food producing animals in the EU, USA and Canada. For these banned substances, the European Commission have established minimum required performance limits (MRPLs) in food, defined as “*minimum content of an analyte in a sample, which at least has to be detected and confirmed*”

[3–5]. Thus, in order to monitor properly these products in aquatic animals, sensitive, fast and accurate analytical methods have to be developed.

Multi-residue analysis of veterinary drugs at trace levels in seafood matrices, such as shrimps, is a challenging task taking into account the inherent complexity of the matrix. The simplification of sample treatment steps (typically previous to mass spectrometry-based measurements) is of great relevance in such applications. The desirable features of alternative methodologies are low organic solvent consumption, reduced labor time and the use of cheaper and disposable material. A variety of sample treatment methodologies have been tested in the last years for the analysis of antibacterial residues in foods [6]. A wide array of the proposed procedures for analyzing veterinary drug residues in food-producing animal tissues employs liquid-phase extraction [7]. Solid-phase extraction (SPE) is the most widely used technique for the clean-up of the extracts. The combination of liquid-phase extraction followed by SPE clean-up step has been satisfactorily applied, for example, to the analysis of several antibacterials in salmon [8] and chicken [9] tissues. Matrix solid-phase dispersion (MSPD) extraction has been also used for the determination of different antibacterials in a

\* Corresponding author. Tel.: +34 953212147; fax: +34 953 212940.

E-mail address: [amolina@ujaen.es](mailto:amolina@ujaen.es) (A. Molina-Díaz).

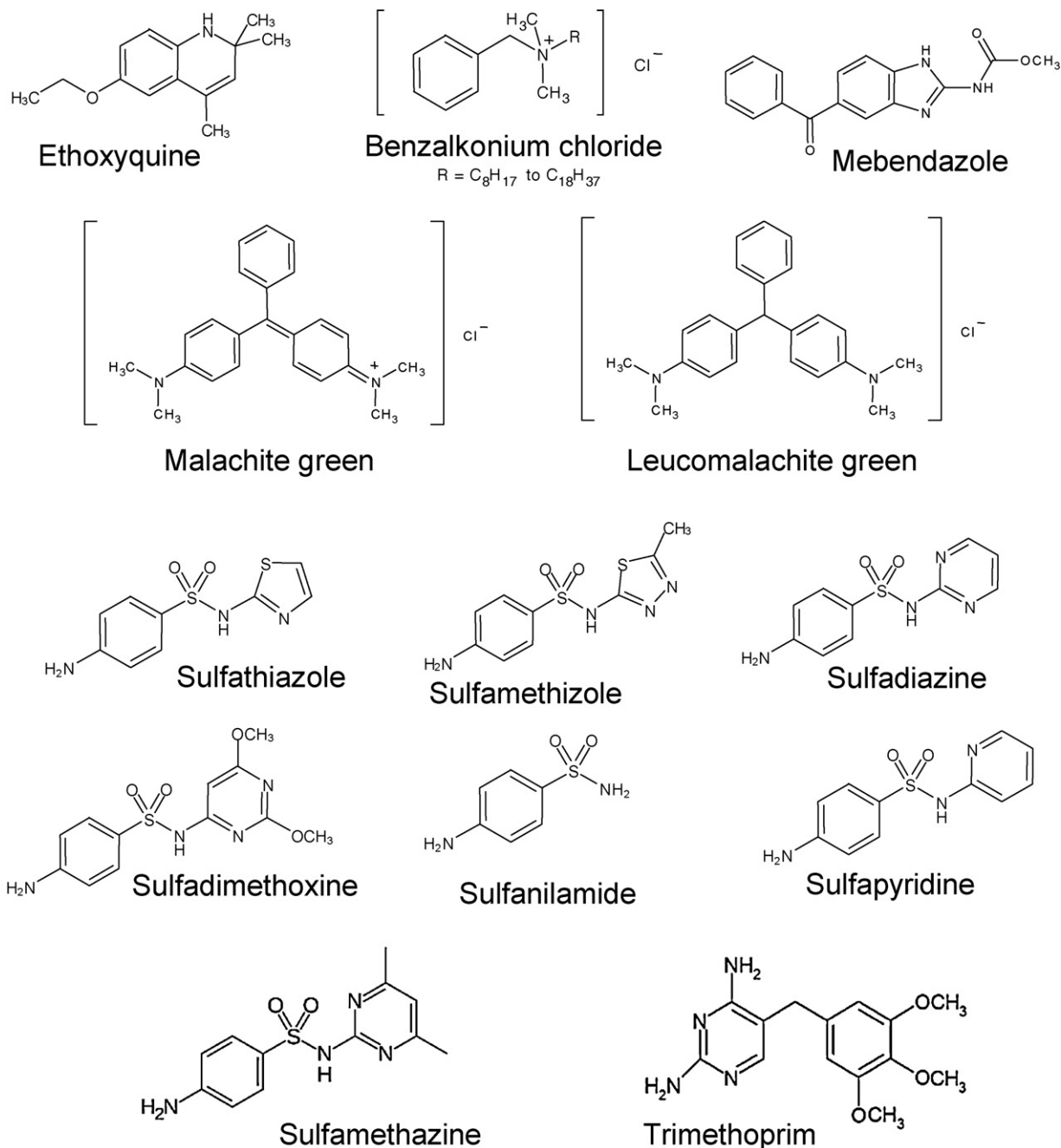


Fig. 1. Chemical structures of the selected multi-class antibiotics.

great variety of foodstuffs [6]. Other methodologies such as pressurized liquid extraction (PLE), microwave assisted extraction (MAE) or solid-phase microextraction (SPME) have also been employed [6].

With regards to the determination step, liquid chromatography has been extensively used for the analysis of veterinary drugs in seafood and fish. Several LC methods have been reported using UV–vis detection and confirmation by mass spectrometry for the determination of MG and LMG in fish and shrimps [10,11], tetracyclines in shrimps [12], or sulfonamides in salmon [13]. Because of the increasingly demanding requirements of sensitivity, liquid chromatography–tandem mass spectrometry (LC–MS/MS), using triple quadrupole MS, is currently the preferred technique for residue analysis of antimicrobials in food [14–18], although

accurate mass full scan MS techniques as time-of-flight mass spectrometry (LC–TOFMS) has also been recently applied [8,19–24].

The aim of this work is to develop an analytical method for the sensitive determination of 13 multiclass antibiotics and veterinary drugs in shrimps using fast liquid chromatography electrospray time-of-flight mass spectrometry. Different sample treatment methodologies based on solid–liquid extraction, solid-phase extraction or matrix solid-phase dispersion have been evaluated for the extraction of the selected chemicals from seafood. Method performance in terms of sensitivity, LODs, linearity and matrix effects has been evaluated in detail. Finally, the proposed method was successfully tested with different samples of different origin purchased in local markets.

Download English Version:

<https://daneshyari.com/en/article/10560505>

Download Persian Version:

<https://daneshyari.com/article/10560505>

[Daneshyari.com](https://daneshyari.com)