Talanta 149 (2016) 103–109

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Quantitative analysis of dicamba residues in raw agricultural commodities with the use of ion-pairing reagents in LC–ESI–MS/MS

Hongyue Guo [a,b], Leah S Riter [a], Chad E Wujcik [a], Daniel W Armstrong [b]

[a] Monsanto Company, St Louis, MO, United States
[b] University of Texas at Arlington, Arlington, TX, United States

ARTICLE INFO

Article history:
Received 22 October 2015
Received in revised form
16 November 2015
Accepted 17 November 2015
Available online 18 November 2015

Keywords:
Dicamba
Ion-pairing reagent
HPLC–MS/MS
Residue analysis
Raw agricultural commodities (RACs)

ABSTRACT

A sensitive and selective HPLC–MS/MS method was developed for the quantitative analysis of dicamba residues in raw agricultural commodities (RACs). Instead of analysis in the traditionally used negative electrospray ionization (ESI) mode, these anionic compounds were detected in positive ESI with the use of ion-pairing reagents. In this approach, only a small amount (60 μM) of a commercially available dicationic ion-pairing reagent was introduced into the post-column sample stream. This method has been validated in six different types of RACs including corn grain, corn stover, cotton seed, soybean, soy forage and orange with satisfactory quantitative accuracy and precision. The limits of quantitation (LOQ) values for these analytes were 1.0 to 3.0 μg/kg. The standard curves were linear over the range of the tested concentrations (3.0 to 500 μg/kg), with correlation coefficient (r) values ≥ 0.999. Evaluation of ionization effects in RAC matrix extracts using diluent blanks for comparison showed no significant matrix effects were present.

1. Introduction

Dicamba (3,6-dichloro-2methoxybenzoic acid), a systematic broad-spectrum auxin-type herbicide, has been used for efficient control of most broadleaf weeds in a variety of crops for more than 40 years [1]. Due to the presence of heterogeneous crop matrix components (i.e., sugar, carbohydrate, starch, macromolecule, pigment, fat and structurally similar compounds), analysis of dicamba residues in RACs can be an extremely challenging task [2]. The polar nature and high water solubility of dicamba residues make their selective extraction and chromatographic resolution from these potentially interfering components very difficult. The diversity of various RAC types and composition further complicates the extraction as each matrix can have unique properties and interfering compounds. Established methods for dicamba residue analysis are based on gas chromatography coupled with electron capture detection (GC-ECD) as adopted by Environmental Protection Agency (EPA) in 1993 [3]. These methods often require an additional sample derivatization step, which at the low concentrations normally has several limitations and often results in irreproducible yields, multiple impurities and an increased analysis time [4]. A variety of other analytical methods also have been developed for the analysis of dicamba residues, including GC–MS [5], enzyme-linked immunosorbent assay [6], micellar electrokinetic capillary chromatography (MEKC) [7], capillary liquid chromatography with UV detection [8], and HPLC coupled with UV [9] or MS detection [2, 10–12]. These methods generally suffered from low sensitivity, which limits their utility for trace residue analysis.

In recent years, HPLC–MS equipped with electrospray ionization (ESI) interface has become the preferred platform for the simultaneous analysis of pesticide residues without derivatization, due to advantages of improved throughput, selectivity, and sensitivity [13]. Generally, applying tandem MS instrumentation (MS/MS) adds further selectivity to the MS detection of compounds in complex RACs. However, analytes with low molecular masses and relatively high polarities pose a general problem to LC–MS/MS sensitivity and selectivity when monitored in the conventionally used negative ESI [14]. These analytes often possess poor ionization efficiency. Impacts on MS sensitivity from often abundant background noise in the low-mass range present additional challenges for low mass dicamba residues. To minimize these factors, we proposed a novel approach with the use of ion-pairing reagent for the sensitive and selective analysis of dicamba residues in RACs. Briefly, it involves the use of specially designed and structurally optimized ion-pairing reagents to pair post-column with the negatively charged analyte [15,16]. The subsequently formed positively charged complexes can be detected and quantified in positive ion mode (see Fig. 1). This technique has several advantages over the routinely used HPLC–MS/MS with negative ESI methods. It moves the detection of analyte from a low m/z region, where the background noise is high, to a higher and more selective m/z region where the background noise is low. Further, the ionization efficiency of the paired analyte is enhanced as shown in

http://dx.doi.org/10.1016/j.talanta.2015.11.043
0039-9140/

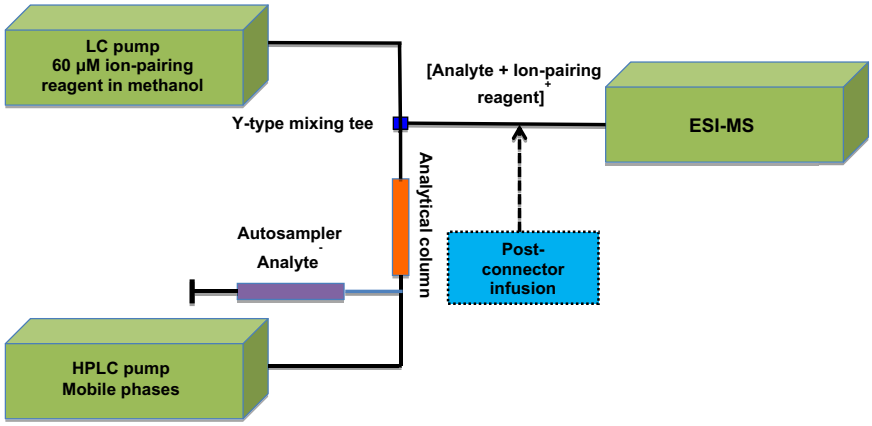


Fig. 1. Instrumental setup of HPLC–ESI–MS/MS. The dotted lines represent the position where the standard solution was infused into the system in the matrix effects evaluation experiments.

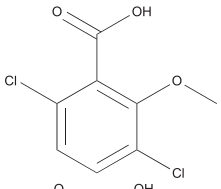
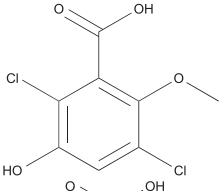
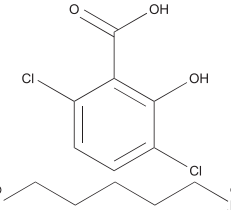
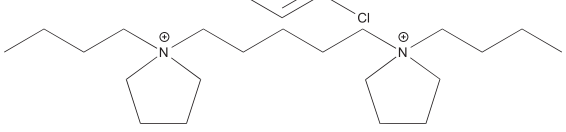
previous mechanism studies [17,18]. In addition, the fragmentation pattern often offers more compound-specific fragment ions for MRM, which eliminates interfering matrix compound peaks and reduces MS background noise. In this work, we evaluated the applicability of using ion-pairing reagent for the sensitive, selective and high throughput analysis of dicamba residues in different types RACs including corn grain, corn stover, cotton seed, soybean, soy forage and orange. Dicamba and its major metabolites, 2,5-dichloro-3-hydroxy-6-methoxybenzoic acid (5-OH dicamba) and 3,6-dichlorosalicylic acid (DCSA) were detected using a commercially available ion-pairing reagent. The developed HPLC–ESI–MS/MS method was validated in terms of method limit of detection (LOD), limit of quantitation (LOQ), selectivity, accuracy and precision in these six different types of RACs. The ionization effects using this method were also evaluated by infusion of a standard solution at the post-connector position and were compared to those of the diluent blank.

2. Materials and methods

2.1. Chemicals and solvents

Analytical standards (> 95%) of dicamba, DCSA and 5-OH dicamba, along with their stable-isotope labeled internal standards: ($^{13}C_6$)dicamba, ($^{13}C_6$)5-OH dicamba and ($^{13}C_6$)DCSA were supplied by Monsanto (St. Louis, MO, USA). Their structures are shown in Table 1. Individual stock standard solutions of 1000 μg/mL were prepared separately with ethanol. The mixed intermediate calibration solution of 1.0 μg/mL was prepared by dilution of the appropriate amount of stock solutions with 1 M hydrochloric acid (HCl) in H_2O. This mixed intermediate calibration solution was used for the preparation of working calibration solutions in the range of 3–500 ng/mL. A mixed internal standard (IS) working solution was freshly prepared at a concentration of 12.5 ng/mL in 50% ACN in acidified water the day to be used for sample preparation. HPLC grade methanol, water and acetonitrile (ACN) were

Table 1
Chemical names, structures and atomic mass units of analytes and ion-pairing reagent used in this study.

Compound name	Abbreviation	Structure*	Atomic mass units
3, 6-dichloro-2-methoxybenzenoic acid	Dicamba		220.0
2,5-dichloro-3-hydroxy-6-methoxybenzoic acid	5-OH dicamba		236.0
3,6-dichlorosalicylic acid	DCSA		206.0
1,5-pentanediyl-bis(1-butylpyrrolidinium)	$C_5(bpyr)_2$		324.3

* Stable isotop-labeled internal standards of the three analytes have six ^{13}C on the benzene ring carbons