Quantitative Analysis of Carbendazim in Orange Juices by Direct Analysis in Real Time (DART®) Mass Spectrometry

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Introduction

Routine pesticide and fungicide use in the United States, as well as abroad warrants the need for analytical techniques that can rapidly screen and quantify residues in order to efficiently sample products before reaching the consumer market. Maximum residue levels (MRLs) for pesticides on fruits and vegetables that are processed into juices are enforced in the US by the US FDA[1] based on criteria set by the US EPA's Code of Federal Regulations[2] and by the European Commission[3] in the EU.

Of particular interest in the United States, carbendazim was found in imported orange juice products from Brazil. There is no tolerance for carbendazim on citrus fruits in the US and any imported citrus products are held to the same regulations. Ambient ionization offers the ability to screen fruit juices and raw produce directly in seconds and with automated sample introduction quantitative measurements have be assessed using direct analysis in real time (DART®) mass spectrometry.

1. http://www.ers.usda.gov/publications/aer827/aer827e.pdf
2. Electronic Code of Federal Regulations. Title 40, Part 180
3. Regulation (EC) No 396/2005 &Regulation (EC) No 149/2008

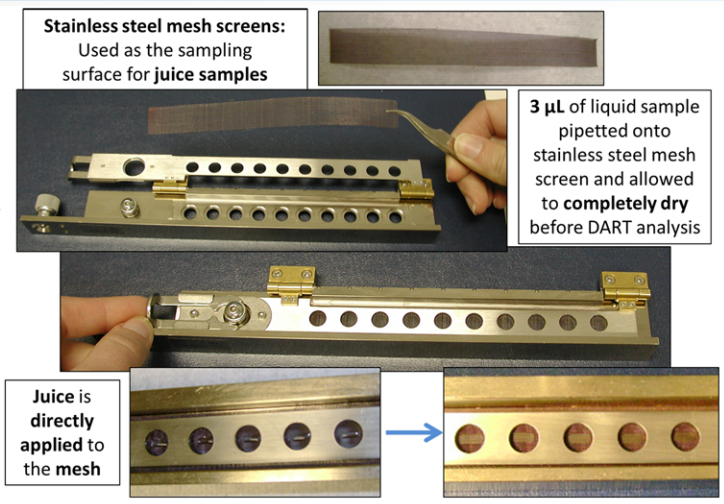


Figure 1. Transmission DART Workflow: Liquid samples are suspended on a metal mesh support for direct DART MS analysis

Methods & Results

A fourth generation standardized voltage and pressure DART ionization source (DART-SVP) was fitted with a motorized linear rail and transmission experiment module. In transmission DART experiments the liquid juices are suspended onto a stainless steel mesh and the heated (250 C) DART ionizing gas passes through the porous sample support efficiently ionizing the analytes. Carbendazim was spiked into orange juice at 1 ppb to 2,000 ppb and orange juices from India, Europe and USA were screened for carbendazim. The DART source was interfaced to an API 4000 QTRAP and Q Exactive Orbitrap benchtop mass spectrometers for a comparative study.

DART-SVP API 4000 QTRAP: MRM Method

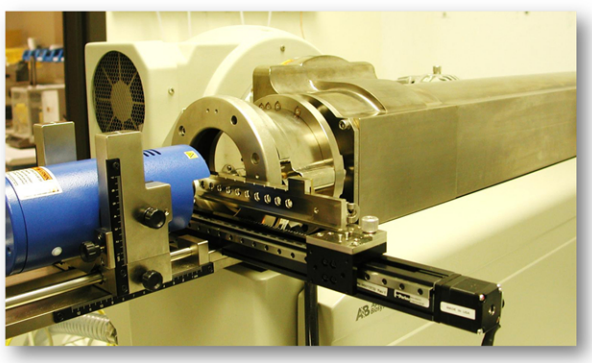


Figure 2. Transmission mode DART coupled to an API 4000 QTRAP for quantitative measurements of carbendazim directly out of undiluted orange juice

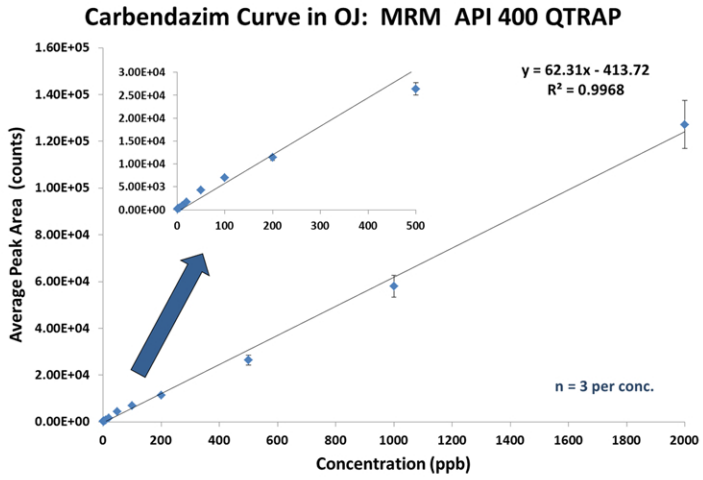


Figure 3. Carbendazim standard curve in orange juice 1 - 2,000 ppb

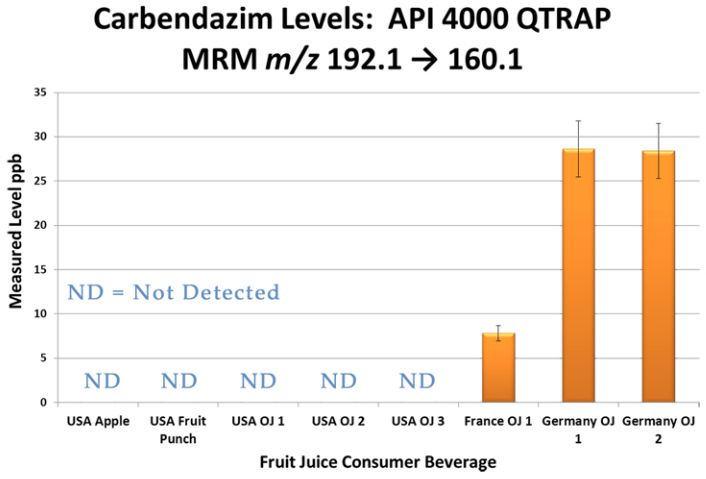


Figure 4. Quantifying carbendazim levels in US and EU orange juices, n = 8 (n = 16 for German)

DART-SVP Q Exactive: Targeted MS² (tMS²)

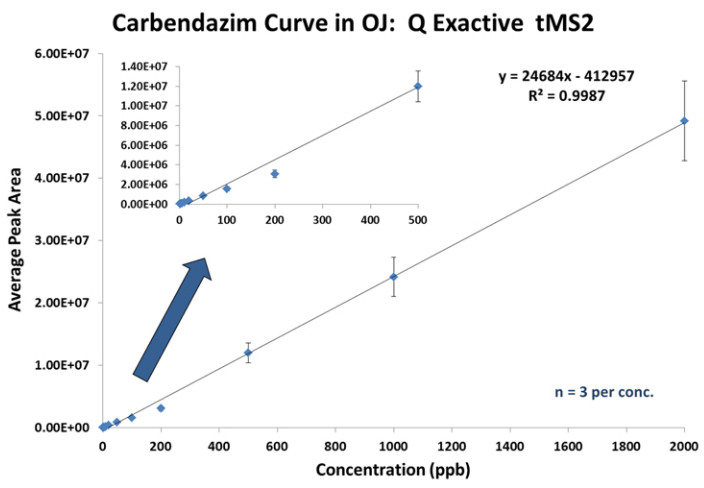


Figure 5. Carbendazim in OJ 1 - 2,000 ppb

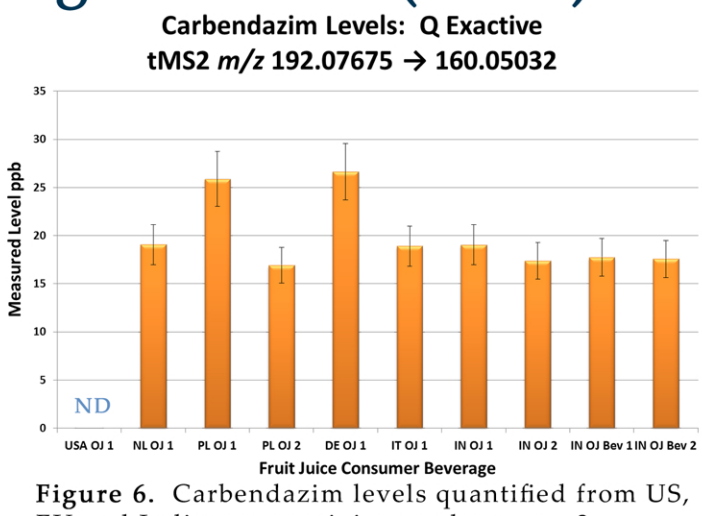
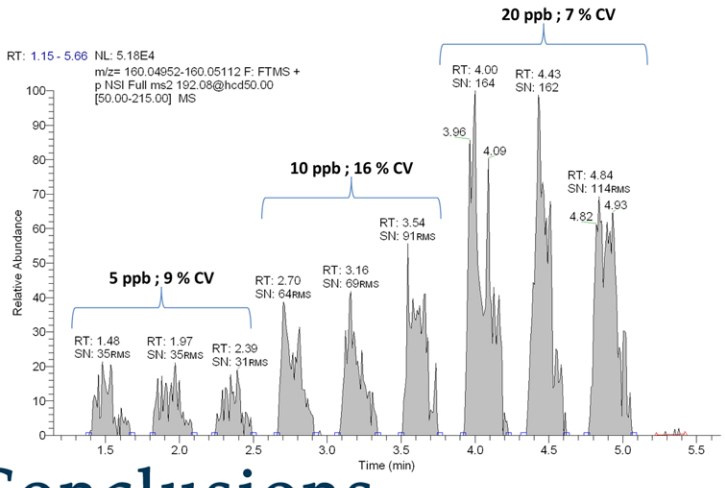
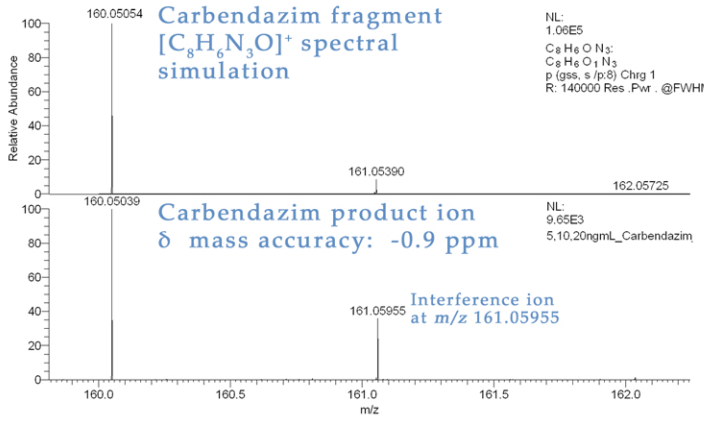
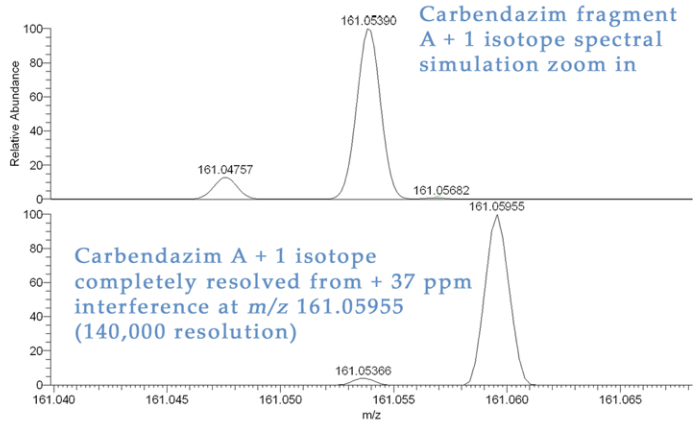


Figure 6. Carbendazim levels quantified from US, EU and Indian orange juice products, n = 3

Figure 7. DART coupled with Q Exactive for targeted high resolution/accurate mass MS/MS experiments







Conclusions

Limits of detection (LOD) and limits of quantitation (LOQ) for carbendazim were 2 ppb and 15 ppb for the MRM experiments and 1 ppb and 2 ppb for the tMS² Orbitrap experiments, where there was a much lower noise threshold.