

## 1 Introduction

A novel enclosed Direct Sample Analysis (DSA) ion source was developed for the direct and rapid analysis of pesticides in different food matrices. The DSA (Direct Sampling Analysis) ionization source utilizes "field free" APCI (atmospheric pressure chemical ionization). Field-free APCI is similar to APCI in that both techniques use a corona discharge needle as an ionization source. However, with the DSA field-free ionization source, the corona needle is fixed in position and shielded within the probe. This places the needle in the optimal position within the vaporized stream for the ionization process and decouples the needle's corona field from the ion entrance field. Consequently, it is very easy to optimize the DSA source, as no mechanical adjustments of the needle or probe position are required, and the electrical field around the ion entrance to the MS is unaffected by the corona field. The enclosed ion source allows programmed control of the reagent ion population, carrier gas species, enthalpy transfer and voltages in ionization and sampling region. Gas entering the ion source during operation can be vented to an exhaust system to avoid exposing the user to vaporized sample. Voltages are applied to the sampling inlet electrodes without exposure to the user during operation. Improved ionization and sampling efficiencies result from a combination of optimized heated gas flow and electric fields in the source and ion transport regions.

Thiabendazole and Imazalil are most widely used fungicides for post harvest treatment of citrus fruits to prevent mold formation in order to preserve the fruit during transport process which may take from several days to several weeks. The maximum residue limits (MRL) of these compounds in USA is 10 ppm. Similarly, the MRL of carbaryl, another pesticide, is 10 ppm in olives. In order to ensure food safety, these fungicides and pesticides in different food matrices need to be monitored. In this work, we explored different sample preparation strategies which require no sample preparation to minimal sample preparation. For measurement of fungicides in citrus food peels, we detected them either directly on peel or by extracting the fungicides from peel with organic solvent. For measurement of pesticides in liquid food matrices such as orange juice and olive oil, the samples were pipetted onto a steel mesh prior to running in a DSA source.

## 2 Method

The enclosed DSA ion source was mounted to a PerkinElmer AxION 2 TOF mass spectrometer (MS). The integral multiple inlet reagent ion generator position was adjustable relative to the sampling and MS entrance. Reagent ion gas composition, flow rate and temperature, countercurrent heated gas flow rate and temperature, and purge gas flow rate were adjustable through software controls.

Solid and liquid samples were introduced into the ion source individually or in batches. They were mounted on a three axis translator with sample position controlled through software. The sample target position was controlled using a three axis translator stage with three linear axis.

For all samples, nitrogen was used as the carrier gas. The reagent ion generator was mounted on a three axis translator to allow optimization of the exit position. Sample was heated through the heated gas delivered from the reagent ion generator. Gas temperature, flow rate and capillary exit voltage was adjusted to maximize signal. PerkinElmer Axion 2 TOF MS was calibrated before any measurement to improve mass accuracy of measurement. The liquid samples were pipetted onto a steel mesh placed between DSA source and TOF MS. The solid surfaces were moved to optimum position between source and TOF MS for measurement with three axis translator.

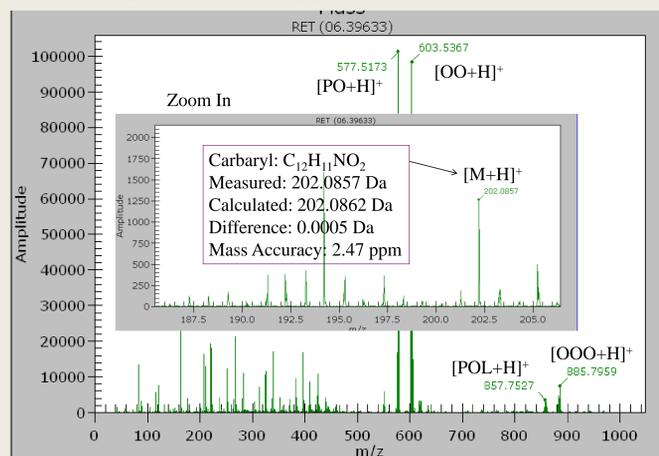
### DSA Source and TOF Parameters:

Corona Current: 4  $\mu$ A  
Nitrogen Gas Temperature: 275 °C  
Capillary Exit Voltage: 70 V  
 $m/z$  40-1000 Da at 5 spectra/s  
Resolution: 12000 at  $m/z = 1000$  Da

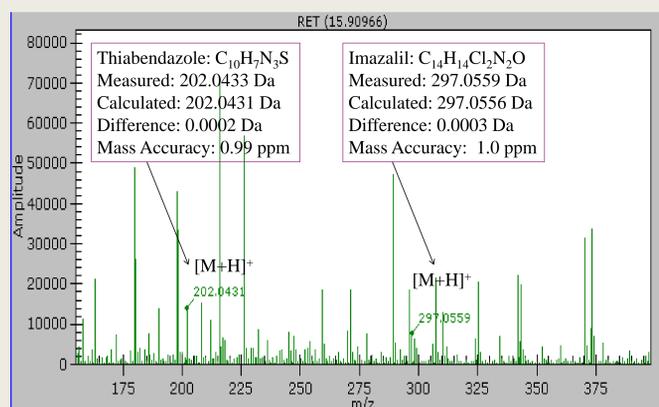
## 3 Results & Discussion



### Mass Spectra of Olive Oil Diluted with IPA 10:1 and Spiked with 10 ppm Carbaryl

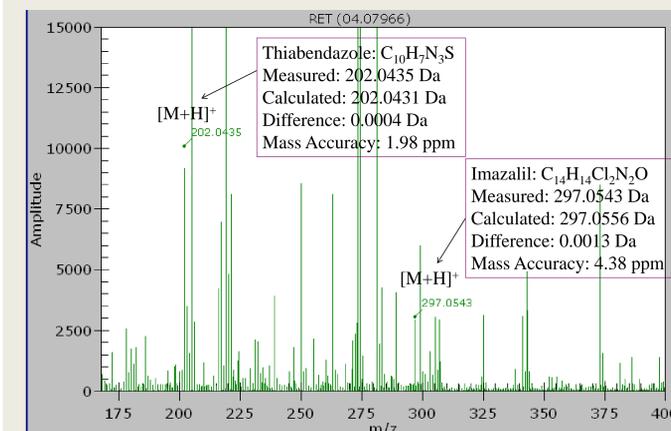


### Mass Spectra of Orange Juice Spiked with 1 ppm Fungicides- Thiabendazole & Imazalil

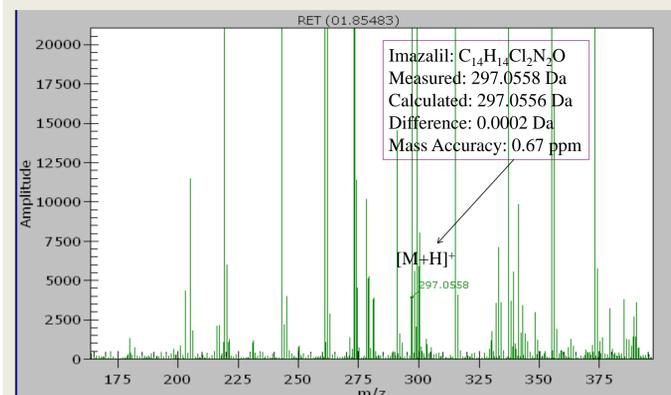


### Mass Spectra for Measurement of Fungicides on Different Citrus Fruit Peels from Local Grocery Store

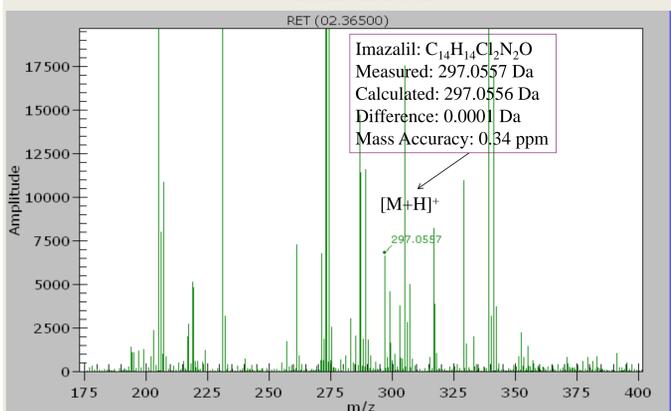
#### Orange Peel



#### Grape Fruit Peel

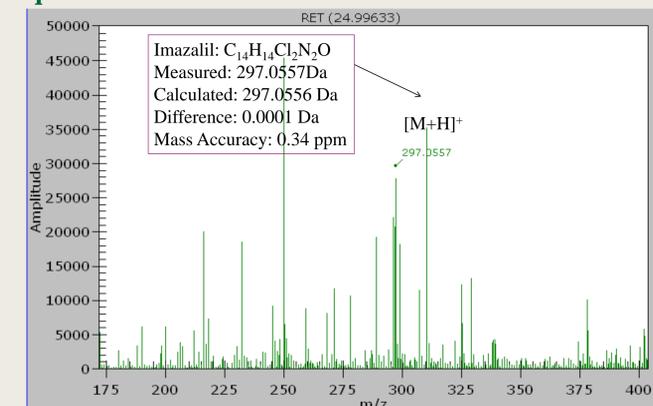


#### Lemon Peel



The measurements with citrus fruits peels from local grocery stores show the presence of fungicides with no sample preparation. Similar measurements (not shown here) with organic citrus fruits showed absence of fungicides.

### Mass Spectra for Measurement of Fungicides from Extract Prepared by 5 gm of Lemon Peel in 10 ml of 40 % Alcohol/Water after Washing Lemon with Dawn Dish Washing Liquid and Water



The extracted sample of washed lemon peel showed presence of fungicides.

## 4 Summary

- DSA source coupled with TOF was able to screen rapidly pesticides at sub-ppm concentration in a number of food matrices, such as olive oil, orange juice and different citrus fruit peels, with minimal or no sample preparation.
- The average mass accuracy of the measurements was 1.5 ppm with external calibration.
- All the measurements performed with DSA source took less than 30 s. Similar measurements with LC/MS system would take 15-30 minutes. This shows higher throughput of DSA source by a factor of 50-100 in comparison to LC/MS systems. In addition, no (or limited) glassware, organic solvents, extraction devices were used with DSA and this greatly reduces the cost per sample compared to a traditional LC/MS approach.
- All citrus fruits obtained from grocery store showed presence of fungicide on their peels where as organic citrus fruits showed absence of them.
- The extracted sample of washed lemon peel showed presence of fungicides.