Direct analysis of dithiocarbamates by ambient mass spectrometry employing a direct analysis in real time (DART) ion source

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Introduction

Dithiocarbamates (DTCs)

- An important class of fungicides widely used in agriculture
- DTC-residue analysis:
  - Hot-acid digestion
  - Determination of formed CS_2
    - Spectrophotometry
    - Head-space GC–MS
    - Head-space SPME–GC–MS
- Specific maximum residue limits (MRLs) are increasingly set by European legislation (**2007/57/EC**) for certain fungicides, to be determined as they are applied: thiram, ziram and propineb

Direct Analysis in Real Time (DART)

- DART represents one of APCI-related techniques employing a glow discharge for the ionisation (**Figure 1**).
- Metastable helium atoms, originated in plasma, react with ambient water, oxygen, or other atmospheric components to produce reactive ionising species.

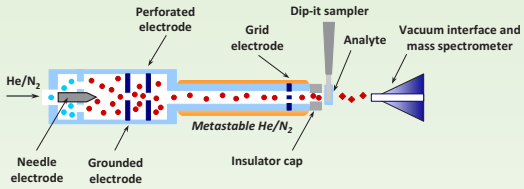

Figure 1: Scheme of DART ion source.

Experimental

- For DART–TOFMS analyses, the system consisting of a DART ion source (IonSense, Danvers, MA, USA), an AccuTOF LP high-resolution TOF mass spectrometer [JEOL (Europe) SAS, Croissy sur Seine, France], and an AutoDART HTC PAL autosampler (Leap Technologies, Carrboro, NC, USA) was used (**Figure 2**).

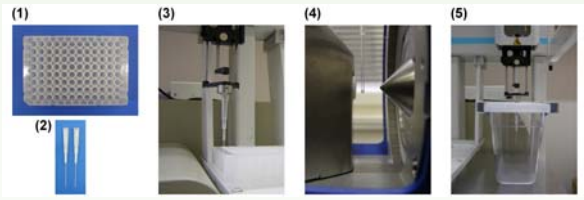

Figure 2: Illustration of automated DART system function.
(1) placing of the sample (extract) to a sampling hole in a tray;
(2) detail of a sampler stick used for sample transfer;
(3) immersion of a sampler stick into the sample for a short time period (4 s);
(4) transfer of a sampler stick with the sample deposited on the surface between the DART ion source and MS inlet, followed by the acquisition of mass spectra for a short time period (5 s);
(5) removal of a used sampler stick, which is then disposed of.

DART

- Ionisation: positive
- Needle electrode: 5,000 V
- Perforated (discharge) electrode: +150 V
- Grid electrode: +250 V
- Helium gas flow: 3.5 L/min
- Gas beam temperature: 300°C
- Desorption time: 5 s

TOFMS

- Acquisition speed: 1 Hz
- Mass range: 100–600 Da
- Peaks voltage: 1,000 V

Extraction step

- An amount of 10 g of homogenised fruit sample were weight into 50 mL plastic centrifuge tube; after addition of 10 mL of MeCN 1 min shaking followed.
- After the addition of 4 g $MgSO_4$ + 1 g NaCl, the tube was shook (1 min) again and centrifuged (5 min, 11,000 rpm) afterwards.

Results

Optimisation of DART–TOFMS instrumental parameters

- In the first phase of the experiments, DART spectra of thiram and ziram were measured in positive ion mode.
- Protonated molecules $[M+H]^+$ were obtained under conditions of DART ionisation. In the case of thiram, the $[M+H]^+$ ion corresponded to an elemental composition of $[C_6H_{12}N_2S_4+H]^+$, while that of ziram to $[C_6H_{12}N_2S_4Zn+H]^+$, each was characterised by the isotope pattern.
- *Gas beam temperature* was tested for 250, 300, and 350°C. The temperature of 300°C provided the highest responses for both analytes tested.
- *Gas beam flow (helium)* was tested for 3.0; 3.5; 4.0; and 4.5 litters per minute. A helium flow of 3.5 L/min gave the highest responses for both analytes tested.
- *Desorption time* was tested for 1, 2, 5, 10, and 30 seconds. It was observed that both target analytes are desorbed within 5 s. Longer desorption time led only to increased detection of various matrix co-extracts present in the extracts.

Detection of thiram and ziram after an extraction step

- For the detection of thiram and ziram in real-life samples, a sample preparation procedure commonly used for pesticide residue analysis (QuEChERS) was tested for pears, apples, and strawberries.
- As illustrated in **Figure 3**, for *quantitative analysis* using a DART ion source, it is necessary to use an internal standard to compensate relatively high variation of the ion intensities of analytes. Triphenyl phosphate (TPP), yielding $[M+H]^+$ at *m/z* 327.10, was used for this purpose (spiked at a level of 2 mg/kg). Calibration plots obtained by analyses of matrix-matched standards (Figure 4) were constructed by plotting the ratio of analyte/internal standard ion intensity *vs.* concentration of the particular analyte. Acceptable linearity was obtained for the tested concentration range; regression coefficients of calibration curves were >0.97.

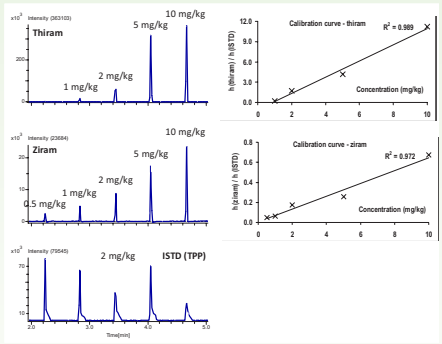

Figure 3: DART–TOFMS analysis of matrix-matched standards (pears) containing thiram (*m/z* 240.996), ziram (*m/z* 304.925), and TPP – internal standard (*m/z* 327.079).

- For the *recovery testing*, the matrix (pears) was fortified at MRL levels by thiram and ziram (*i.e.* 5 mg/kg and 1 mg/kg, respectively) and also by internal standard (triphenyl phosphate) to 2 mg/kg.
- The recoveries obtained by this method were 85.2% and 82.7% for thiram and ziram, respectively, with repeatability of 6.7% and 8.9%, respectively (expressed as relative standard deviation, RSD, %). The limits of quantification (expressed as the lowest calibration levels) were 1 mg/kg and 0.5 mg/kg for thiram and ziram, respectively.

Conclusions

- Fast and rapid method for determination of thiram and ziram in fruit based on QuEChERS extraction was developed.
  - Crude extract is immediately analysed employing ambient MS with DART–TOFMS.
  - Analysis time is reduced significantly:
    - <8 min for sample preparation
    - <1 min for extract examination by DART

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